INFLUENCE OF DISSOLVED ORGANIC MATTER (DOM) ON MERCURY SPECIATION AND REACTIVITY IN RAINWATER

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ABSTRACT

This study focused on determining interactions between dissolved organic matter (DOM) and mercury (Hg) in rainwater, and their significance in affecting the transport and reactivity of mercury in the environment. Photochemical, UV oxidation, and rain - river mixing experiments were also performed to investigate their influences on mercury behavior. Concentrations of total, total dissolved, particulate, labile (reactive), hydrophilic total dissolved and hydrophilic labile mercury were determined in Wilmington, North Carolina rainwater. Volume weighted averages and standard deviations of 32.2 ± 3.3, 24.7 ± 2.5, 5.1 ± 1.1, 14.8 ± 2.0, 13.0 ± 1.6, and 7.8 ± 2.0 pM respectively. Dissolved gaseous mercury was detected at low levels in 40% of samples. Non-labile and hydrophobic fractions of Hg were on average 40 and 53 % respectively, indicating that strong complexes between Hg and DOM exist in rainwater in relatively large percentages. Glutathione did not outcompete Hg in these complexes, suggesting that some Hg-DOM complexes are very strong. Labile mercury concentrations in photochemical experiments increased after 6 hours of irradiation relative to dark controls suggesting light may be contributing to the production of labile Hg complexes. Photochemistry experiments with unfiltered rain yielded inconsistent results that were different from filtered experiments, indicating that particulate mercury plays a variable role in photochemical processes. Labile mercury measured over 6 hours in river water spiked with rain water did not rapidly form strong Hg-DOM complexes with river water DOM suggesting this process does not occur or that it is relatively slow, and light did not influence this. Intense UV oxidation of rain prior to addition of bromine monochloride (BrCl) to ensure total DOC oxidation may result in greater total mercury concentrations and also indicates the presence of organic mercury complexes in rain.

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INTRODUCTION

Mercury (Hg) is a ubiquitous contaminant which enters the environment from a variety of natural and anthropogenic sources. Natural sources include soil, vegetation and volcanoes, whereas anthropogenic sources are mainly solid waste incineration, coal combustion, metal smelting, chlor-alkali plants and gold mining. Earlier studies have focused on measuring total Hg concentrations (THg; operationally defined as the Hg present in unfiltered acidified rain samples) and indicate there is a significant quantity present in wet deposition, even at locations far removed from anthropogenic sources. However, quantifying THg concentrations does not fully elucidate the behavior of atmospheric Hg because its reactivity and subsequent toxicity are critically dependent on its speciation. A much more relevant assessment of the redox behavior and environmental impact of Hg in atmospheric waters can be obtained when levels of individual Hg species are measured.

Mercury exists in three oxidation states, 0, +1 and +2, with the +1 state being very unstable and therefore rarely found in the atmosphere (Schroeder & Munthe, 1998, Lin & Pehkonen, 1999). Mercury in its elemental, gaseous state (Hg^0) is released by natural and anthropogenic sources. In this form, mercury is very stable and has a half life of 0.5-2 years in the atmosphere (Schroeder & Munthe, 1998, Lin & Pehkonen, 1999). Because Hg^0 is relatively unreactive and has a long atmospheric residence time, it is capable of traveling great distances from where it originated, explaining its presence worldwide. Particulate mercury, Hg(II), and Hg(II)(aq) are less stable in the atmosphere and are emitted by anthropogenic sources (Selin & Jacob, 2008). Their atmospheric residence times are only days or weeks. Many species of Hg(II) are very water soluble and therefore are deposited in rain relatively close to their

anthropogenic sources. Particulate mercury is also deposited close to the emitting sources via both wet and dry deposition. Rainwater contains all three forms of atmospheric mercury but is dominated by Hg(II) species.

Hg interacts strongly in surface waters with dissolved organic matter (DOM) (Ravichandran 2004). Mercury binds to reduced-sulfur sites in DOM, which are present in very small amounts, although the ratio of reduced-sulfur to total mercury in aquatic environments is still very high. Hg-DOM complexes dominate the speciation of Hg under most environmental conditions, except under high salinity or sulfidic conditions (Ravichandran 2004). As a result of this strong association, Hg-DOM complexes are a major control on the fate and transport of Hg in the environment. It is not known what mercury is complexed to in rainwater. Based on the concentration of DOM and chloride in rainwater, likely species present in rainwater include inorganic complexes, such as Hg-chloride and Hg-hydroxides, as well as Hg-DOM complexes. Complexation constants for Hg-DOM interactions in surface waters have been determined but the applicability of these constants to rainwater is not known since the atmospheric DOM has different chemical properties than surface water DOM (Gordon, 2006). It is important to understand DOM interactions with Hg in rain because it could influence the speciation, solubility, mobility and/or toxicity of mercury in rain. It will also be important in predicting the reactivity of mercury when it enters surface waters because it could drive photooxidation/reduction reactions or methylmercury production.

There is no method to directly measure Hg-DOM complexes, so several indirect approaches are needed in order to investigate the presence of Hg-DOM interactions in rainwater. One approach is to measure labile, or reactive, mercury complexes in rainwater. Labile mercury is defined as all mercury species reducible by stannous (II) chloride reduction (Bloom, 1994).

Labile mercury complexes include inorganic Hg complexes and some weak Hg-DOM complexes (Mason et al., 1992). What is more important when examining Hg-DOM interactions, is the fraction of mercury that is not labile since the mercury species are strongly complexed most likely to DOM. Labile mercury has been measured in rainwater (Ebinghaus et al, 1999, Lamborg et al., 1995, Mason et al., 1992, Mason et al., 1997). Hammerschmidt et al. (2007) compiled Hg data from several different studies across North America and found that labile mercury complexes were correlated to the amount of methylmercury in rain, suggesting that they play a role in methylating mercury in the atmosphere.

Another approach to investigate Hg-DOM complexes in rain involves measuring the amounts of hydrophilic and hydrophobic Hg fractions through solid-phase extraction using C_{18} cartridges. Extractions using C_{18} fractionate DOM into two operationally defined fractions: the hydrophobic fraction, which is retained by the cartridge and the hydrophilic fraction, which passes through the cartridge. These extractions are potentially useful in examining Hg complexation since the hydrophobic fraction should only contain Hg-DOM complexes. The combination of C_{18} extractions and labile Hg measurements provides two independent means to examine the presence of Hg-DOM complexes in rainwater.

Extractions using C_{18} cartridges can be coupled with glutathione (GSH^{3-}) titration to investigate the strength of Hg-DOM complexes. This method has been used previously in wastewater effluent and surface waters (Hsu & Sedlak 2003, Hsu-Kim & Sedlak 2005) to investigate the strength of Hg(II)-complexing ligands. However, the previous studies used samples amended with Hg at levels three orders of magnitude higher than what is naturally present in rainwater. Using this method to measure the complexation strength in rainwater will enable a comparison between the relative strength of Hg-DOM in rainwater and surface waters.

This is crucial, since it is likely that Hg-DOM complexes are driving photochemically mediated reactions in rainwater and the reactivity of rainwater Hg when it enters surface waters.

An important uncertainty in the study of Hg speciation in rainwater concerns the mechanisms involved in controlling its speciation. One set of processes which most likely influences Hg speciation in rainwater involves photochemical transformations. These could include photoreduction of organically complexed Hg(II) (Zhang and Lindberg, 2001), photoreduction of Hg(II) in the presence of organic acids and Fe(III) oxides (Lin and Pehkonen, 1997), aqueous phase reduction of Hg(II) by photochemically produced hydroperoxy radicals (Lin and Pehkonen, 1999), and photodecomposition of methylmercury in the aqueous phase (Gardfeldt *et al.*, 2001). An examination of photochemical reactions of mercury in rainwater is crucial to understanding its chemical speciation in rainwater, which in turn is essential in understanding the reactivity of rainwater Hg upon its mixing with surface waters.

The research presented in this thesis examines the speciation and reactivity of mercury in rainwater. A comprehensive examination of the different Hg species including total mercury, dissolved mercury, gaseous mercury, labile mercury and C_{18} extractable mercury was undertaken. This speciation data was compiled with ancillary rainwater data such as pH, anions, DOC and hydrogen peroxide concentrations to understand factors controlling the distribution of Hg species in rainwater. The data was also used to examine the presence and strength of Hg-DOM complexes in rainwater. Rainwater was further examined using photochemical experiments to examine the photoreactivity of Hg in rainwater. While the reactivity of Hg in surface waters has been extensively studied, very limited data is available on the reactivity of Hg in rainwater. Rainwater provides an important source of Hg to many aquatic environments.

Therefore, the data presented in this thesis enhances the understanding of the reactivity of newly deposited Hg to surface water environments.

METHODS

Rainwater Collection

Rainwater was collected on the University of North Carolina Wilmington (UNCW) campus on an event basis from April 2007 to July 2008. The UNCW rainwater collection site is a large open area, approximately one hectare, within a turkey oak, long leaf pine and wiregrass community, typical of inland coastal areas in southeastern North Carolina. This rainwater site (34º13.9'N, 77º52.7'W) is on the UNCW campus, approximately 8.5 km from the Atlantic Ocean. Due to the close proximity of the sampling location to the laboratory, analyses or storage procedures could be initiated within minutes of collection, which reduced the possibility of compositional changes between the time of collection and analysis. Real-time precipitation maps were used to initiate the sampling process.

Event rainwater samples were collected using four Aerochem-Metrics Automatic Wet-Dry Precipitation Collectors. One collector contained a 4 L muffled Pyrex glass beaker from which samples for dissolved organic carbon, hydrogen peroxide, pH and inorganic ions were collected. The other collectors for trace metal samples held a HDPE funnel leading through Teflon lined acid cleaned tubing to a 2.2 L Teflon bottle and were cleaned using a modification of Bruland's trace metal clean procedures (1979). Mercury blanks were performed on the rain site collectors by passing Milli-Q (MQ), (ultra-pure (>18 MΩ) water produced by a Plus Ultra-pure water system (Millipore, Bedford, MA)) through the rain collection setup and were less than 1 pM Hg.

Storm Trajectory Determination

Precipitation events were categorized using air-mass back-trajectories generated using version 4 of the Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) developed at the National Oceanic Atmospheric Administration – Air Resources Laboratory (NOAA/ARL). Trajectories were generated using a stand-alone PC version of the model and calculated using pre-processed gridded horizontal and vertical wind fields generated at 6-h intervals from the National Center for Environmental Prediction's Global Data Assimilation System using the Medium Range Forecast model to produce the forecast wind fields. Single back-trajectories were run for each measured precipitation event collected at UNCW starting at the recorded conclusion of precipitation. Trajectories were generated for a 120 h hind-cast at the 500 meter level. Events were classified using method described in Kieber et al. (2005).

Sample Bottles

All mercury samples were stored in Nalgene polyethylene terephthalate copolyester (PETG) bottles. These bottles were cleaned in 25% HNO_3 for 24 hours, rinsed three times with DIW (deionized water), then stored in 10% HCl for at least 24 hours before use. Just before use, bottles were rinsed five times with MQ. Blanks on these bottles were performed by adding MQ which was preserved and run the same as samples, described in the mercury analysis section.

Teflon bottles were used for photochemistry experiments to maximize light penetration and to reduce loss of mercury to the sides of the bottles. Perfluoroalkoxy (PFA) Teflon bottles were used for photochemistry experiments because they have been shown to be less porous than

fluorinated ethylene propylene (FEP) Teflon bottles (Whalin, 2007). Teflon bottles were cleaned using a three step cleaning protocol involving the sequential soaking of the bottles in 1M KOH for 24 hours, 16M HNO_3 for 24 hours, and stored in 10% HCl for at least 24 hours prior to use. They were rinsed extensively with DIW between acid cycles and with MQ just before use (Parler, 2005).

Reagents and Standards

Reagents used for mercury analysis were trace metal grade materials from VWR, J.T. Baker, Aldrich Chemical, or Fisher Scientific, unless otherwise noted. All solutions were prepared using MQ. All reagents were prepared in trace metal clean bottles using trace metal clean procedures.

Mercury analysis was performed using a modification of the purge and trap method described in Bloom (1994). A 0.9 M (20% weight/volume) stannous (II) chloride solution was prepared in a 20% HCl solution. A 0.27 M bromine monochloride (BrCl) solution was prepared in a fume hood by dissolving 1.1g of reagent grade KBr and 1.6g reagent grade $KBrO_3$ in a solution of 20 mL MQ water and 80 mL of 12 M trace metal grade HCl (T-HCl). This reagent was used to preserve samples for total and total dissolved mercury analysis. A 30 % hydroxylamine hydrochloride solution (4.3 M) in MQ was prepared and purified by addition of 0.9 M $SnCl_2$ solution described above (1mL/L) and purging at least two hours at 500 mL min^{-1} with UHP argon to remove Hg.

The stock Hg standard, (Fluka) contained 4.99mM mercury as $Hg(NO_3)_2 \cdot H_2O$ and was stable for one year or until the expiration date (USEPA Method 1631). The secondary Hg

standard of 4.99µM was a dilution of the stock standard. It had BrCl added at 5% of the solution volume and remained stable for 6 months. The working Hg standard of 4.99nM was a dilution of the secondary standard. It had BrCl added at 1% of the solution volume and remained stable for 1 month.

Sample Preservation and Preparation

Dissolved gaseous mercury (DGHg) samples were unfiltered, unaltered and were processed immediately after collection (Lindberg, 2000). Labile Hg samples were passed through 0.2µm acid cleaned Supor hydrophilic polyethersulfone membrane filters. Labile Hg samples were also processed immediately, as it is not stable in solution (Bloom, 1994). Total dissolved mercury samples were passed through 0.2 µm acid cleaned Supor hydrophilic polyethersulfone membrane filters. These filters were cleaned by soaking in 10 % HCl for 24 hours, then rinsed 5 times with MQ and stored in MQ. Total mercury samples were not filtered. Total mercury and total dissolved mercury samples were stored in trace metal clean 125 mL PETG bottles. Bromine monochloride was added to the samples to reach a concentration of 0.5% BrCl to oxidize organic matter in the sample. The BrCl solution contained 80% HCl so additional acidification of the samples was not required. Samples were run within three weeks, as samples have been shown to be stable within this time (Parler, 2005).

Sample Analysis

Mercury in its elemental form was analyzed using purge and trap, desorption and cold vapor atomic fluorescence spectrometry (CVAFS), using a Tekran Model 2600 Mercury Analysis System. Because the instrument can only detect mercury in its gaseous elemental form (Hg^0), each separate species of mercury analyzed involved different sample preparation to reduce the species of mercury desired into Hg^0. A calibration curve was prepared daily with standards ranging from 1 to 24 pM and the sample volume used for analysis was adjusted to fall within the calibration range.

Dissolved gaseous Hg is the measurement of Hg^0 naturally present in a sample; therefore no reducing agent was required for this analysis. For this analysis, 250 mL of sample was used. It was crucial that the bubblers used during DGHg measurements never contained $SnCl_2$ in order to avoid the production of Hg^0 during analysis. From this point, the Hg^0 was purged from the sample using ultra-high pure (UHP) argon gas for 20 minutes. The stream of gas containing Hg^0 was passed through a soda lime trap to remove moisture and the Hg^0 was amalgamated onto a gold-coated sand column. The gold column was removed from the purging set-up and placed in a manifold where the Hg was thermally desorbed. This was done using a nichrome coil controlled by a Brooks Rand Model 2 temperature controller. The coil heated for 3 minutes to reach a temperature between 450-500º C. The Hg was then carried into an inert gas (UHP argon) stream into the quartz cell of the spectrometer for detection. Light from a low-pressure 4-W mercury vapor lamp was directed through the quartz cell at a wavelength of 253.7 nm and excited the mercury atoms which emit light at intensity proportional to the concentration of mercury passing through the cell. This emitted light passed through a filter and into a

photomultiplier tube, converting the light into an electrical signal, which was integrated by Logger Pro software. The detection limit and percent relative standard deviation for this and other mercury species analyzed in this study are in Table 1. The detection limits were determined by multiplying the standard deviation of the blanks for each method by three, and then dividing by the average slope of the calibration curves.

Labile Hg is defined as all $SnCl_2$ reducible Hg species in a sample (Bloom, 1994). For this analysis 50-125 mL of sample was added to the bubblers and MQ water was added to bring the final volume in the bubblers to 125 mL. The labile Hg in the sample was reduced using 500 µL of 0.9 M $SnCl_2$ reagent as described above, the sample was purged, and the rest of the analysis was carried out as described above.

Total mercury (THg) and total dissolved mercury (TDHg) are defined as all BrCl-oxidizable mercury species found in an unfiltered and filtered aqueous solution respectively. Total mercury includes Hg(II), Hg^0, organo-complexed Hg(II) compounds, particulate Hg, and some covalently bound organo-mercurials (USEPA Method 1631). Total dissolved mercury is the same, without particulate Hg species, as they are removed via filtration. Particulate mercury (Hg_{part}) was determined by subtracting TDHg from the total mercury in the sample. Since samples had the addition of BrCl when collected, hydroxylamine hydrochloride was added just prior to analysis to reduce excess BrCl which could interfere with Hg detection. For this analysis 50-125 mL of sample was added to the bubblers and MQ water was added to bring the final volume in the bubblers to 125 mL. The Hg in the sample was reduced using 500 µL of 0.9 M $SnCl_2$ solution, the samples was purged, and the rest of the analysis was carried out as described above.

Calibration

A calibration curve was prepared each day the instrument was used. The bubblers used for calibration and analysis were 250 mL Pyrex glass gas washing bottles, 24/40 jointed with a modified glass joint, which fitted into the bubbler with a glass tube extending from the gas inlet at the top of the stopper and ended in a 15º angled frit near the bottom of the bubbler. An outlet extended from the top where the columns were connected. These bubblers were used to purge rainwater samples of gaseous, elemental mercury (Hg^0) through soda lime traps to remove moisture onto gold sand columns for analysis. The bubblers were stored in 10 % HCl between uses.

The calibration curve for all mercury analyses was made using one working standard, (4.99 nM Hg^{2+}). On days where only dissolved gaseous mercury samples were run, calibration blanks were made by adding 125 mL of MQ into 250 mL bubblers. On days where only labile mercury samples were measured, calibration blanks were made by adding 500 µL of 0.9 M $SnCl_2$ solution to 125 mL of MQ in 250 mL bubblers. On days where only total and total dissolved mercury samples were measured, calibration blanks were made by adding 500 µL of 0.9 M $SnCl_2$ solution, 500 µL of BrCl solution, and 150 µL of $NH_2OH{\cdot}HCl$ solution to 125 mL of MQ in 250 mL bubblers. A curve was prepared ranging from 0.125 to 2.994 pmol and ensured that the curve encompassed the range of the samples, which were diluted accordingly.

C_{18} Analysis

Hydrophobic complexes are retained by the resin in C_{18} cartridges. By determining the total dissolved mercury before and after passing solutions through a C_{18} cartridge, the concentration of hydrophilic mercury complexes can be measured directly. The concentration of hydrophobic mercury complexes was determined by subtracting the hydrophilic mercury concentration from the total dissolved mercury concentration. Sep-Pak® Plus C_{18} cartridges (Waters Corporation, Milford, MA) were used for C_{18} experiments. Each C_{18} cartridge was cleaned by sequentially passing 10 mL HPLC grade methanol, 20 mL 1 M T-HCl in methanol mixed 9:1, and 20 mL MQ through the cartridge (Hsu et al, 2003). Once a cartridge was cleaned, 50 mL of a filtered rainwater sample was passed through it in an Hg-clean vacuum apparatus. Each cartridge was only used for one sample and then discarded. TDHg was determined on the fraction of the Hg that passed through the cartridge and was defined as hydrophilic Hg (Hsu & Sedlak, 2003) which was compared to TDHg in unfractionated samples. To test the background level of Hg associated with this extraction procedure, MQ alone, and synthetic rain water (SRW), which is MQ with the addition of H_2SO_4 to adjust the pH to 4.5 (a typical pH of rainwater), were passed through a clean cartridge and analyzed for TDHg. Table 2 shows the C_{18} blank information. A t-test showed that the two columns in Table 2 are not statistically different ($p = 0.678$).

Table 1: Detection Limits (DL) and % relative standard deviation (% RSD) for mercury species analysis.

	DL (pM)	% RSD
THg/TDHg	0.1	4.6
Labile Hg	0.1	5.8
Hydrophilic Hg	0.8	6.5
DGHg	0.1	5.8

Table 2: C_{18} cartridge blanks (pM), before (TDHg) and after (Hydrophilic TDHg) being passed through a cartridge. MQ = Milli Q water, SRW = Synthetic Rain Water, ND = Not Detected

	TDHg (pM)	**Hydrophilic TDHg (pM)**
MQ	1.1	1.0
	3.3	4.3
	1.6	1.1
	1.6	0.4
	1.6	3.0
SRW	0.9	0.9
	ND	0.5
	2.8	3.0
	2.8	3.9
	2.8	2.8

Competitive Ligand Exchange Titrations

Competitive ligand titrations coupled with extraction were performed in order to investigate the binding strength of Hg(II) species in rainwater. This method has previously been used in wastewater effluent samples that had been spiked with large concentrations (1.1-1.3 nM) of Hg (Hsu & Sedlak, 2003) but this is the first attempt at applying this method to samples containing natural levels of Hg (pM). The titrations used glutathione (GSH^{3-}) which forms hydrophilic complexes that are not retained by C_{18} cartridges. By titrating with this ligand, the binding strength for mercury(II) complexes in rainwater can be estimated.

A stock solution of 5.0 mM glutathione (reduced free acid form) was made for titration experiments. A working standard was made daily by diluting the stock standard to produce 50.0 µM GSH^{3-}. This solution was added to rainwater samples to reach concentrations in the range of 5 - 100 nM GSH^{3-}. The samples were equilibrated for 1-2 hours before use (Hsu et al, 2003) and were then passed through C_{18} cartridges and analyzed for TDHg. Comparison of TDHg with and without GSH^{3-} showed the effect of GSH^{3-}.

Photochemistry Analysis

Photochemistry experiments were conducted on rain events as soon after collection as possible, within 24 hours. Photolyses were performed using a Spectral Energy Corp. solar simulator (LH 153 lamp housing, 1 kW Xe arc lamp, LPS 256 SM power supply) equipped with an AM1 filter to remove wavelengths not found in sunlight. The spectral quality and intensity of the solar simulator is very similar to that of midsummer, noon-time solar irradiance for 34°N

latitude (Kieber et al., 2003). Temperature was controlled by a water bath kept at 25 °C ± 3 ºC. Measurements of UVA, UVB, and photosynthetically active radiation (PAR), with wavelengths of 400-700 nM, were taken before irradiation of samples.

Each rain event was divided into three aliquots for initial, dark and light measurements. Filtered and unfiltered rainwater samples in 250 mL PFA Teflon bottles were filled with no head space for photolysis experiments. Samples were irradiated or kept in the dark (control) for 6 hours. Samples were periodically rotated to ensure even distribution of light among all samples. Analyses for TDHg, labile Hg and in some cases DGHg were performed on samples before and after irradiation.

Intense UV Oxidation

Selected rainwater samples were exposed to intense UV oxidation to destroy all organic material in the sample, including potential ligands for Hg binding. This high-energy UV light was generated by a 1.2 kW high-pressure Hg vapor lamp (Ace Glass, Vinelad, NJ), and samples were irradiated for 6 hours. Samples were prefiltered, acidified with T-HCl at 0.5% of sample volume, placed in quartz tubes with Teflon caps and sealed with Teflon tape to prevent Hg contamination. Also, blanks were measured before and after UV oxidation to ensure there was no Hg contamination during the UV oxidation process.

RESULTS AND DISCUSSION

Method Comparison

An earlier study conducted in our lab suggested that dissolved gaseous Hg (DGHg) was an important component in rainwater (Parler, 2005). Between 18 and 37 percent of total Hg in rainwater was thought to be present as DGHg and this species was shown to increase after rainwater was exposed to light (Parler, 2005). One of the initial objectives of my study was to replicate DGHg measurements in whole and irradiated rainwater. Inconsistencies were found between the results obtained by Parler (2005) and my study, resulting from an analytical error in the previously reported results because DGHg was in much lower concentrations in this study.

The primary difference in the two analytical methods involved treatment of the glass gas washing bottles (bubblers) which are used during the purging step in the DGHg analysis. Dissolved gaseous Hg analysis is performed by adding 250 mL of a rain sample into a bubbler. The sample is purged of DGHg (Hg^0) for 20 minutes with UHP argon and the Hg^0 is trapped onto a gold-coated sand column. The Hg^0 sorbed onto this column is then thermally desorbed under a UHP argon stream and detected with a Tekran model 2600 CVAFS. To obtain a standard curve, inorganic mercury is added to a bubbler as Hg(II) and reduced to Hg^0 by the addition of 20% $SnCl_2$ in 20% HCl (0.9 M $SnCl_2$ in 2.4 M HCl). Once the Hg(II) is converted to Hg^0 the remainder of the analysis is the same as performed for the DGHg. The same bubblers were used for standards curves and DGHg sample analysis in the Parler (2005) study. Separate bubblers were used for standards and DGHg sample analysis in order to avoid $SnCl_2$ contamination of DGHg bubblers in my study. When two samples were run this way, DGHg

was below the detection limit of 0.1 pM for the DGHg method (Figure 1). When the same samples were run using the method from Parler (2005), high and inconsistent DGHg values were found (Figure 1). Six replicates were run on a synthetic rainwater sample spiked with inorganic mercury which had no DGHg present. The Parler (2005) method for DGHg was used, and values ranged from below detection to 11.4 pM, with an average of 3.7 pM (± 4.8 pM), (Figure 2). Residual $SnCl_2$ in the bubblers was likely responsible for the high DGHg values presented in the previous study (Parler, 2005) because Sn^{2+} is a reductant for Hg^{2+} present in rain samples.

DGHg values reported by Parler (2005) do not reflect accurate DGHg concentrations in rainwater, but are more likely similar to labile or reactive Hg measurements. Labile Hg is measured by adding a known amount of $SnCl_2$ reagent to the water sample, resulting in reduction of the reactive fraction of Hg(II) to Hg^0. Mercury complexes that are easily reduced by $SnCl_2$ are considered labile Hg complexes. Adding $SnCl_2$ reagent in amounts lower than used in the labile Hg analysis method reported in this paper yielded variable results (Figure 3). While the residual amount of $SnCl_2$ on bubblers in Parler (2005) is not known, it was likely less than what is used for labile Hg analysis, therefore the apparent DGHg values in Parler (2005) can only be used as preliminary results for my labile Hg study.

The results found in Parler (2005) were useful, as they gave a starting point for the current study. Parler (2005) found a strong positive correlation between the concentrations of apparent DGHg and chloride in rain and a strong negative correlation between the apparent DGHg and DOC concentrations in rain. When rain was irradiated the apparent DGHg concentration increased relative to initial and dark control concentrations. These trends gave a starting point for my labile Hg research.

Figure 1: Concentration of DGHg using bubblers that never contained $SnCl_2$ (clean bubblers, black bars) and bubblers that previously contained $SnCl_2$ (dirty bubblers, white bars). Analysis was conducted on two separate collections of one rain event, E690A and E690B. Error bar indicates magnitude of standard deviation based on duplicate analyses. E690B was analyzed one time.

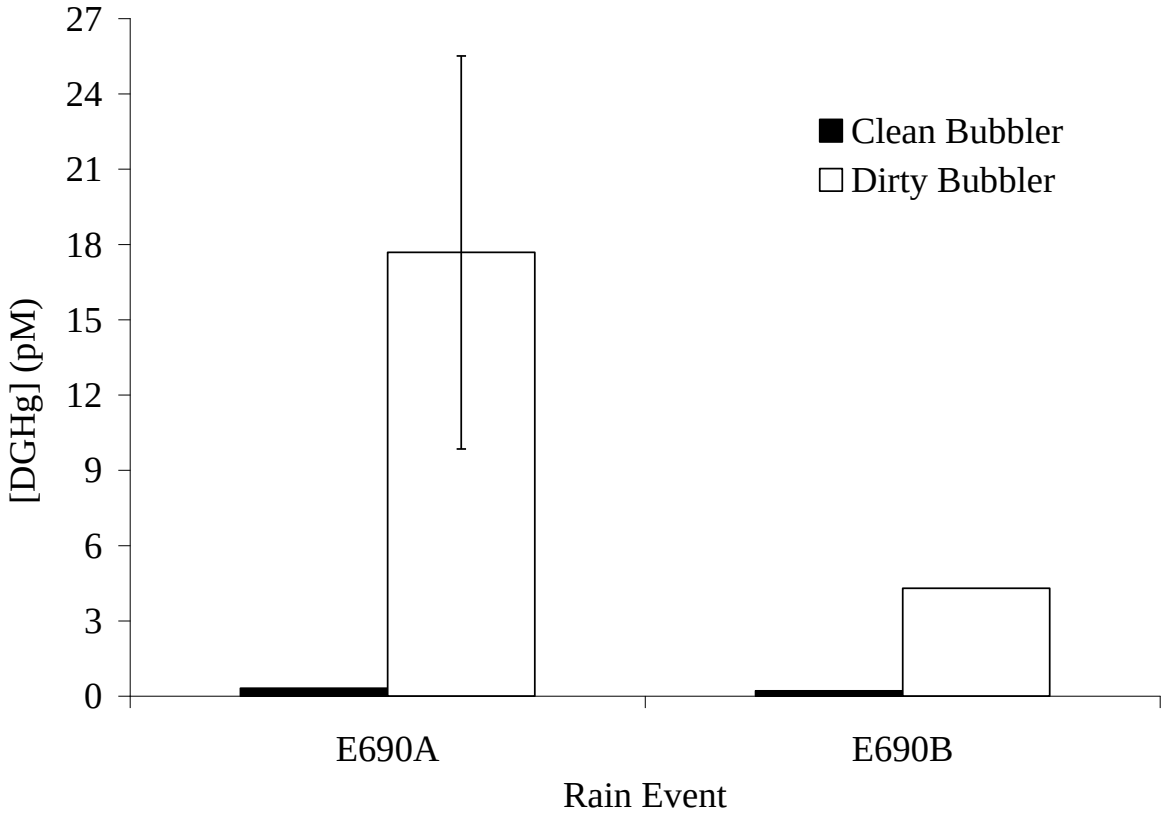


Figure 2: Concentration of DGHg on replicates (n=6) and two total dissolved mercury replicates on a synthetic rainwater sample amended with 10 pM inorganic mercury. Samples for apparent DGHg were run using the Parler (2005) method, using bubblers with residual $SnCl_2$.

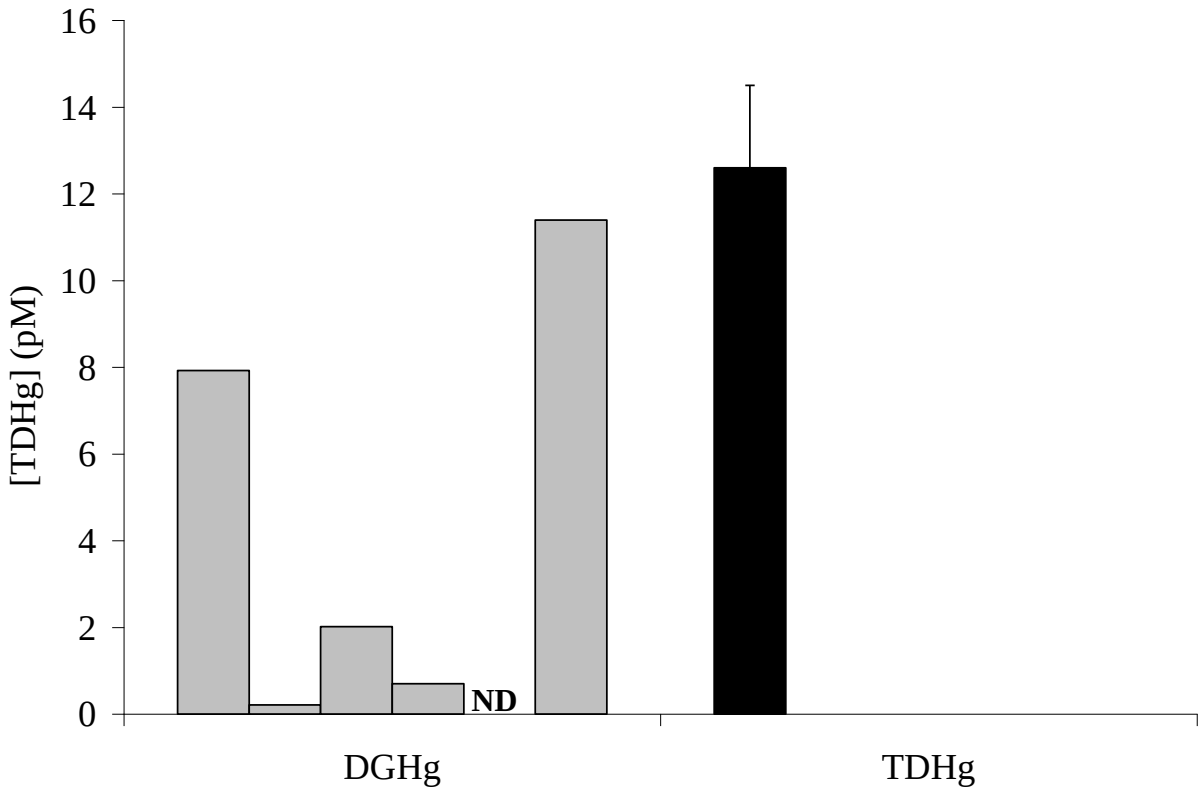
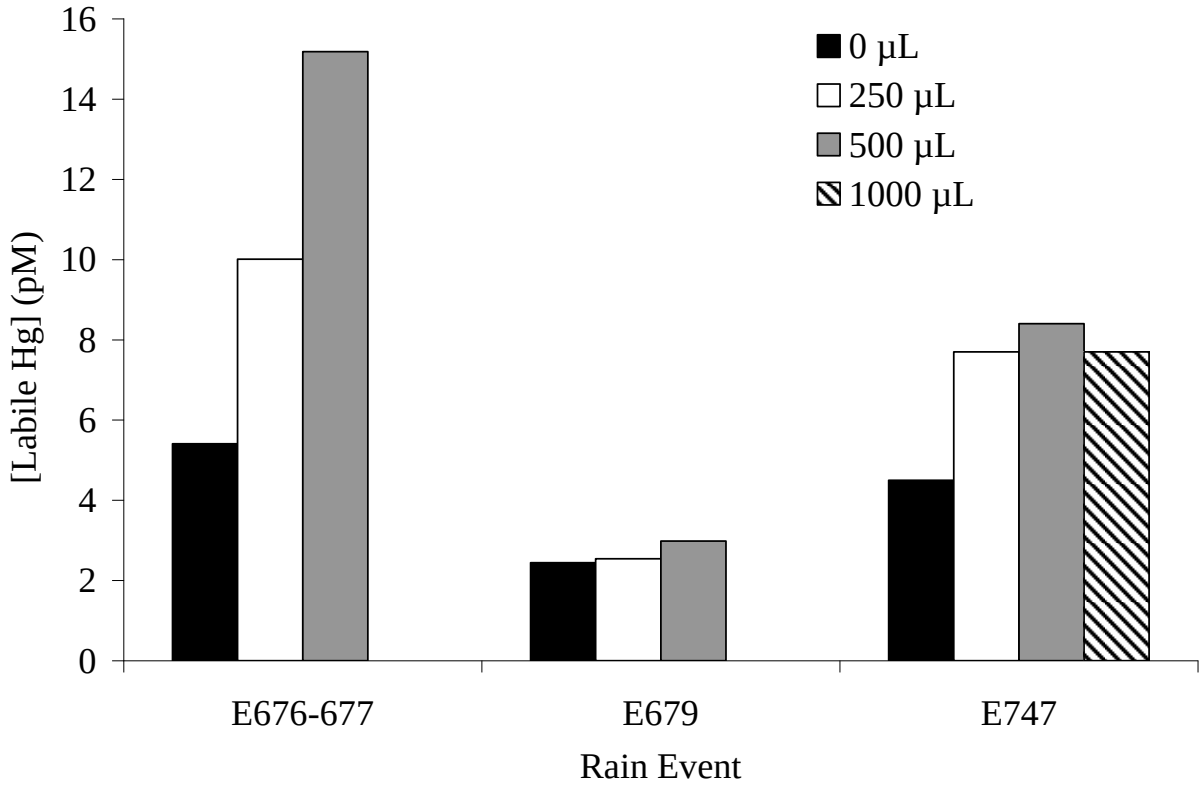


Figure 3: Labile Hg concentrations as a function of 0.9 M $SnCl_2$ reagent added (µL). Analyses were conducted on three rain samples, a mixture of E676 and E677, E679, and E747.



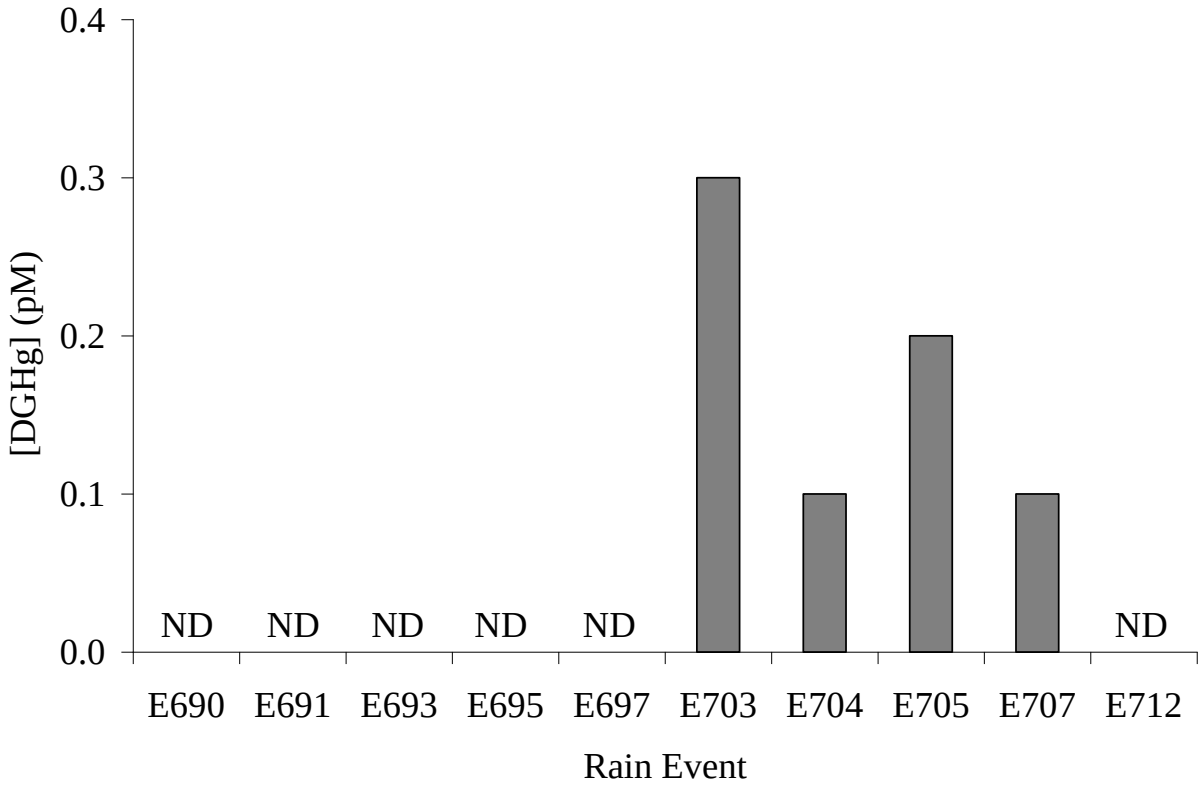
Concentration and Speciation

Dissolved Gaseous Mercury

DGHg was measured in ten rain events with clean bubblers between April 15th, 2007 and September 27th, 2007 (Fig 4). The analysis was performed immediately after cessation of precipitation so that DGHg did not have time to degas from solution. Four of the events had DGHg values above the detection limit of the method (0.1 pM) while the rest did not have DGHg in detectable concentrations.

Mercury in its gaseous, elemental phase (Hg^0) is the predominant form of Hg in the atmosphere (Schroeder & Munthe, 1998, Lin & Pehkonen, 1999), but it is not very water soluble. Gaseous mercury has an equilibrium value of 0.02 pM, assuming a gas phase concentration in the northern hemisphere of 10 pmol m^{-3} (Morel et al., 1998) and a Henry's Law constant of 9.3 x 10^{-2} M atm^{-1} at 15°C, which is predicted based on scavenging of Hg^0 from the gas phase. Lin and Pehkonen (1999) calculated a similar equilibrium value estimate, ranging from 0.013 – 0.053 pM. When detectable, DGHg was probably supersaturated and hence unstable with respect to degassing, so values in figure 4 are likely underestimates. The significantly larger than equilibrium gas phase concentration of DGHg in the aqueous phase suggests an aqueous phase production mechanism. There are several proposed mechanisms for DGHg production in natural waters, including photochemical reactions in the presence of DOM and/or Fe or Mn, secondary photoreduction of Hg(II) complexed to DOM (Tseng et al, 2004), and microbial reduction of Hg(II) (Siciliano et al., 2002).

Figure 4: Dissolved gaseous mercury concentrations (pM) in ten unaltered fresh rain events. Each value has been blank corrected.



Other Mercury Species

Rainwater was collected in Wilmington, North Carolina from 31 rain events between August 22nd, 2007 and July 11th, 2008. The number of events sampled represents 50% of the total number of storms during this time interval and 56% of the rain by volume. The remainder of rain events were not sampled because they either did not have sufficient volume for successful Hg analysis, or they could not be sampled quickly enough for speciation analysis. All 31 rain events were analyzed for labile Hg and total dissolved Hg (TDHg), and 26 of the events were also analyzed for total Hg (THg). Particulate Hg (Hg_{part}) was calculated as the difference between THg and TDHg. Hydrophilic TDHg was analyzed for 21 rain events, and hydrophilic labile Hg was collected for 7 of those events.

Volume weighted averages for all mercury species are reported in Tables 3 through 5. A flow chart demonstrating how the various mercury species are related is presented in Figure 5. Approximately 84% of THg was TDHg and about 16% was Hg_{part}. This was similar to previous results from this location, where 77% of THg was TDHg from September 2005 through September 2005 (Parler, 2005), although the volume weighted average of THg was smaller in this study (32.2 pM vs. 45.5 pM). This is also very similar to what Selin and Jacob (2008) determined for mercury deposition in North America based on their model, finding 89% of THg as TDHg and 11% as Hg_{part}. Poissant and Pilote (1998) found values of 74% of THg as TDHg for rain in southern Quebec.

Approximately 60% of TDHg in this study was labile Hg, which falls within the range of other precipitation studies, including 64% labile Hg on average in Atlantic Ocean rain (Lamborg et al., 1999), 47% labile Hg on average in northern Wisconsin rain (Lamborg et al., 1995), and

70% labile Hg on average in Pacific Ocean rain (Mason et al., 1992). Labile mercury is important to measure in rainwater because it provides information about Hg-DOM complexes. The fraction of a sample that is not labile is most likely Hg-DOM complexes, suggesting at least 40% of the Hg exists in this form. This is an underestimate because some of the labile fraction of mercury in rainwater can be weaker Hg-DOM complexes. Labile, or reactive, mercury measurements are also important to measure because they have been correlated to methylmercury concentrations in rainwater (Hammerschmidt et al., 2007), and could also potentially play a role in photochemical oxidation/reduction processes.

Approximately 47% of TDHg was hydrophilic while 48% of labile Hg was hydrophilic labile Hg. Hydrophilic mercury results are explained in further detail in a later section. All the percentages reported on mercury species in this study were based on volume weighted averages for the subset of samples that had measurements for both species being compared, not based on the volume weighted averages in Tables 3 through 5.

Tables 3, 4 and 5 also show how the species varied with differing seasons and storm trajectories. Winter was defined as all storms measured between December 21st and March 20th, while summer was defined as all storms measured between June 20th and September 22nd. The mercury species in general had higher volume weighted averages in summer compared to winter, which has been observed in many other precipitation studies (Guentzel et al., 2001, Glass and Sorenson, 1999, Sorensen et al, 1994, Selin and Jacob, 2008). This pattern could be attributed to scavenging of Hg(II) from upper altitudes by deep convection in the summertime over southeastern North America (Selin and Jacob, 2008). Labile mercury had almost exactly the same volume weighted average concentrations for summer and winter, but the total deposition of labile Hg in summer was greater than that in the winter (2.4 and 1.9 picomoles respectively),

indicating that season does has an effect on labile mercury deposition. The deposition of mercury removes rain volume as a variable, and compares only picomoles of mercury deposited during those storms. There was no significant difference between summer and winter events for any of the mercury species measured in this study (t-tests, table 6).

Rain events were subdivided as either marine, continental, or mixed to determine how Hg speciation was affected by air mass back trajectory (tables 3 and 4). Contrary to what was observed at this location in a previous study (Parler, 2005), all mercury species had higher volume weighted average concentrations in marine storms compared to terrestrial storms. The deposition per event for all Hg species was also higher in marine storms compared to terrestrial storms, ranging from 1.1 to 7.8 times higher in marine storms. However, because this dataset is so small with high variability, these differences are not significant (t-tests, table 6). One particular marine storm, E735, had up to 5 times more total Hg than other marine storms and this contributed to the high variability of the dataset. However, the trajectory for this storm (Figure 6) shows that the air mass traveled very close to the coast of Florida while the other marine storms did not get this close to land. This suggests that the mercury in E735 may have been influenced by mercury in the air coming from Florida. This idea is supported by the National Atmospheric Deposition Program/Mercury Deposition Network's data which shows that Florida had the highest annual total mercury concentration and wet deposition of any state on the east coast in 2007, indicating that there is a history of high mercury deposition in that area (NADP, 2008). Every storm that passed through or near Florida in this study did not have unusually high Hg concentrations, but it is possible that E735 picked up some Hg from this area.

The time of day that a rain event occurred was found to be related to the concentration and percent of labile mercury in rain (Tables 7 and 8). The time of day was split into four time

periods; 12AM-6AM, 6AM-12PM, 12PM-6PM, and 6PM-12AM. However, there were only enough events during the 12AM-6AM and 12PM-6PM time periods to make a comparison. The beginning and end of each rain event occurred within the time period; any events that overlapped time periods were not included. There were not enough data to compare THg or hydrophilic Hg. TDHg did not vary significantly with time of day (t-test, $p = 0.389$). Labile mercury concentration and the percent labile of TDHg were significantly higher during 12PM-6PM compared to 12AM-6AM (t-tests, $p < 0.1$, $p < 0.01$ respectively), suggesting that photochemical processes increase labile Hg concentrations in rain. This is directly investigated through rain photochemistry experiments in this study.

Table 3: Volume weighted average concentrations (pM) and volume weighted standard deviations of TDHg and labile Hg species in rainwater collected in Wilmington, NC between August 22nd, 2007 and July 11th, 2008. n = number of rain events. Amount = amount of rain in mm. % Labile Hg is the percent TDHg that was labile.

	n	Amount	TDHg	Labile Hg	% Labile Hg
All Data	31	525	24.7 ± 2.5	14.8 ± 2.0	59.9%
Summer	6	120	27.7 ± 3.2	14.2 ± 3.3	51.3%
Winter	14	214	22.0 ± 3.4	14.1 ± 2.8	64.1%
Terrestrial	3	31	22.0 ± 5.5	14.1 ± 3.6	64.1%
Marine	6	133	23.1 ± 5.6	15.0 ± 4.9	64.9%

Table 4: Volume weighted average concentrations (pM) and volume weighted standard deviations of THg and Hg_{part} species in rainwater collected in Wilmington, NC between August 22nd, 2007 and July 11th, 2008. n = number of rain events. Amount = amount of rain in mm. % Hg_{part} is the percent THg that was Hg_{part}.

	n	Amount	THg	Hg_{part}	% Hg_{part}
All Data	26	420	32.2 ± 3.3	5.1 ± 1.1	15.8%
Summer	5	105	35.9 ± 4.6	7.9 ± 3.5	22.0%
Winter	14	214	24.4 ± 4.3	2.6 ± 1.2	10.7%
Terrestrial	3	31	26.6 ± 7.1	4.6 ± 1.2	17.3%
Marine	3	58	38.2 ± 8.0	3.5 ± 2.1	9.2%

Table 5: Volume weighted average concentrations (pM) and volume weighted standard deviations of hydrophilic Hg species in rainwater collected in Wilmington, NC between December 16th, 2007 and July 11th, 2008. n = number of rain events. Amount = amount of rain in mm. All of the hydrophilic labile Hg data was from the winter, so a seasonal comparison was not available.

	n	Amount	Hydrophilic TDHg	n	Amount	Hydrophilic Labile Hg
All Data	21	381	13.0 ± 1.6	7	167.4	7.8 ± 2.0
Summer	4	89	14.0 ± 1.2	--	--	--
Winter	12	206	10.0 ± 2.1	--	--	--

Figure 5: Flow chart of mercury species measured in this study.

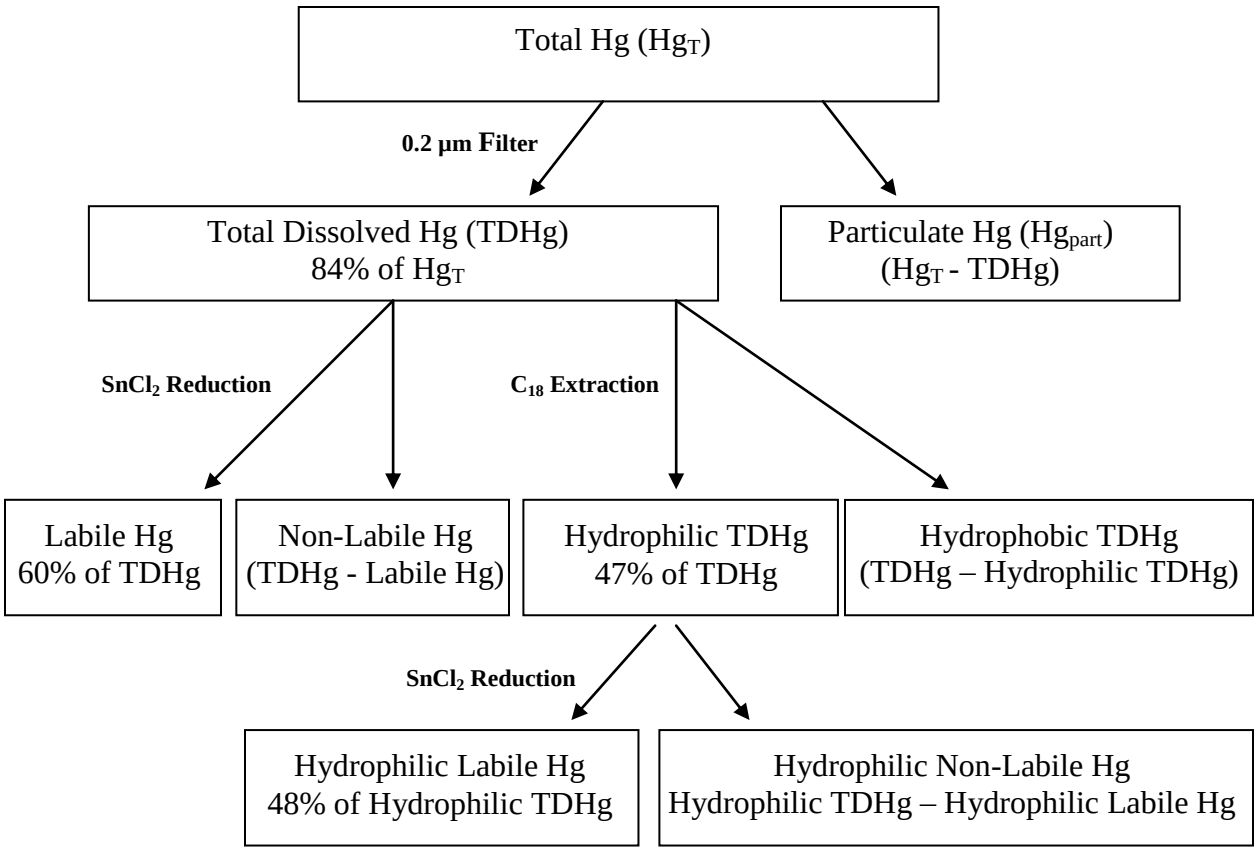


Table 6: p values from t-tests for various mercury species against storm seasons and trajectories.

	THg	TDHg	Hg_{part}	Labile Hg	Hydrophilic TDHg
Winter vs. Summer	0.160	0.638	0.089	0.807	0.293
Marine vs. Terrestrial	0.352	0.844	0.730	0.860	0.370

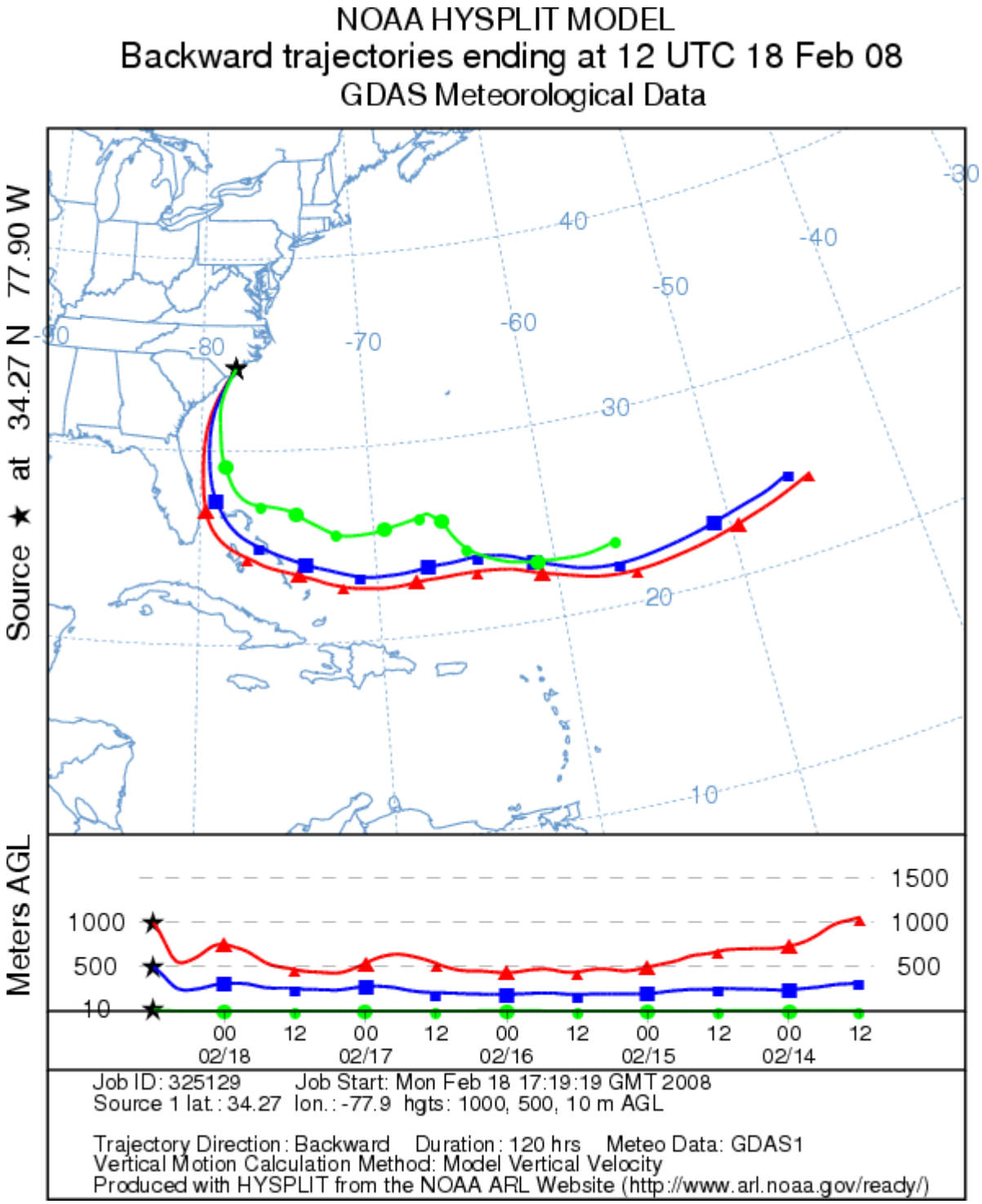
Table 7: TDHg and labile Hg concentration (pM) and % labile Hg as a function of time of day rain events occurred. % labile Hg is of TDHg.

Time of Day	Rain Event	TDHg (pM)	Labile Hg (pM)	% Labile Hg
12AM - 6AM	E705	25.0	7.5	30.1
	E715	20.4	8.3	40.7
	E730	19.9	9.7	48.8
12PM - 6PM	E718	22.2	14.1	63.4
	E720	27.9	21.8	78.1
	E733	12.8	10.3	80.4
	E737	36.7	28.4	77.2
	E746	19.5	13.6	69.6
	E765	30.3	15.4	50.9
	E767	41.4	33.2	80.2

Table 8: Average TDHg and labile Hg concentrations (pM), % labile Hg and standard deviations as a function of time of day rain events occurred. % labile Hg is of TDHg. n = number of samples

Time of Day	n	TDHg (pM)	Labile Hg (pM)	% Labile Hg
12AM - 6AM	3	21.7 ± 2.8	8.5 ± 1.1	40 ± 9.4
12PM - 6PM	7	27.3 ± 9.9	19.5 ± 8.5	71 ± 11.0

Figure 6: Storm back trajectory for E735. This shows where the air masses came from 120 hours prior to the rain event originating at 10 (green), 500 (blue), and 1000 (red) meters.



Correlation Analysis

Pearson correlations were used to examine the relationship between different rainwater parameters. During this study, concentrations of hydrogen ion, dissolved organic carbon (DOC), nitrate and non-seasalt sulfate (NSS) were highly intercorrelated with each other ($p < 0.001$), as has been observed previously in rainwater from this and other locations, and concentrations of hydrogen peroxide were weakly correlated with DOC and NSS ($p < 0.04$). This indicates that rainwater collected during this study was similar to rainwater collected during other studies in this location. Patterns of correlation were also investigated among the various mercury species and other rainwater analytes as well as rain amount. Many correlations were found among the mercury species. Because TDHg and Hg_{part} are the primary contributors to THg, they are highly correlated to THg (Table 9). TDHg and Hg_{part}, however, were not correlated with each other (Table 9) as observed previously (Parler, 2005). TDHg was highly correlated with hydrophilic TDHg and Labile Hg (Table 9). Labile Hg was also highly correlated with THg, and weakly correlated with hydrophilic labile Hg ($p < 0.02$) (Table 9). Hydrophilic TDHg and hydrophilic labile Hg were strongly correlated as well ($p < 0.01$) (Table 9).

Hydrogen peroxide was correlated with TDHg and Hg_{part} ($p < 0.03$), driven predominantly by a strong correlation of hydrogen peroxide to THg ($p < 0.01$) (Table 10). None of the mercury species significantly correlated with rain volume (Table 10). A previous study at this location did find that TDHg and THg correlated with rain volume. To compare these studies, data from this study was combined with previous rain data from this location (Figures 7 and 8). The lack of a significant correlation in this study comes from the absence of rain events with THg concentrations greater than 80 pM which also contributes to the lower volume

weighted THg concentration in this study. There were also no rain events with volume greater than 60 mm in the current study. Without these extremes, the washout pattern was not observed in this study as in the previous study. None of the mercury species significantly correlated with concentrations of hydrogen ion, dissolved organic carbon, non-seasalt sulfate, or chloride, nitrate, sulfate, or oxalate ions, suggesting that these are not controlling mercury distributions in rainwater at this location (Table 11). A severe drought occurred during the first half of this study, which could have had an effect on mercury concentrations, speciation and patterns of correlation.

Table 9: Pearson correlation coefficients, probability of significance, and number of samples for correlations between THg, TDHg, Hg_{part}, Labile Hg, Hydrophilic TDHg and Hydrophilic Labile Hg.

	TDHg	**Hg_{part}**	**Labile Hg**	**Hydrophilic TDHg**	**Hydrophilic Labile Hg**
THg	0.895 <0.001 26	0.518 0.007 26	0.846 <0.001 26	0.865 <0.001 21	0.675 0.096 7
TDHg	----	0.082 0.691 26	0.948 <0.001 31	0.965 <0.001 21	0.774 0.041 7
Hg_{part}	----	----	0.051 0.807 26	0.071 0.759 21	0.036 0.939 7
Labile Hg	----	----	----	0.916 <0.001 21	0.849 0.016 7
Hydrophilic TDHg	----	----	----	----	0.902 0.006 7

Table 10: Pearson correlation coefficients, probability of significance, and number of samples for correlations between mercury species and other rainwater analytes. Volume is the event rain volume.

	Volume	Peroxide	H^+	DOC
THg	-0.118 0.566 26	0.496 0.010 26	0.033 0.873 26	0.199 0.329 26
TDHg	-0.064 0.733 31	0.405 0.024 31	0.116 0.536 31	0.181 0.329 31
Part. Hg	-0.278 0.170 26	0.444 0.023 26	-0.012 0.954 26	0.146 0.475 26
Labile Hg	-0.055 0.769 31	0.341 0.060 31	0.038 0.840 31	0.073 0.696 31
Hydrophilic TDHg	-0.010 0.965 21	0.315 0.165 21	0.186 0.419 21	0.239 0.297 21
Hydrophilic Labile Hg	0.437 0.327 7	0.064 0.891 7	-0.462 0.297 7	-0.379 0.401 7

Table 11: Pearson correlation coefficients, probability of significance, and number of samples for correlations between mercury species and other rainwater analytes.

	Cl^-	NO_3^-	SO_4^{2-}	NSS	Ox^-
THg	-0.175 0.414 24	0.315 0.133 24	0.249 0.241 24	0.274 0.195 24	-0.013 0.953 24
TDHg	-0.138 0.474 29	0.321 0.090 29	0.259 0.175 29	0.279 0.143 29	0.067 0.729 29
Part. Hg	0.061 0.776 24	0.298 0.157 24	0.227 0.287 24	0.189 0.375 24	-0.047 0.828 24
Labile Hg	-0.087 0.656 29	0.229 0.233 29	0.237 0.215 29	0.245 0.200 29	0.007 0.970 29
Hydrophilic TDHg	-0.209 0.390 19	0.323 0.177 19	0.199 0.413 19	0.240 0.323 19	0.138 0.573 19
Hydrophilic Labile Hg	-0.031 0.954 6	-0.719 0.107 6	-0.492 0.321 6	-0.428 0.398 6	-0.157 0.767 6

Figure 7: Combined TDHg data from previous rain study and current rain study at this location. The grey diamonds are data from the previous study (Parler, 2005), and the black squares are from the current study.

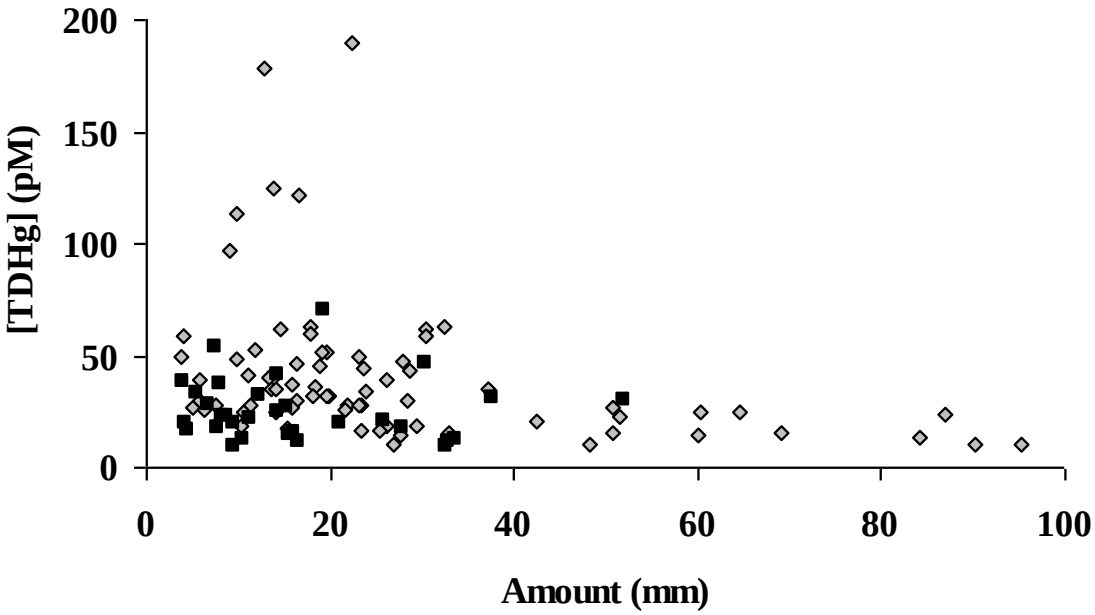
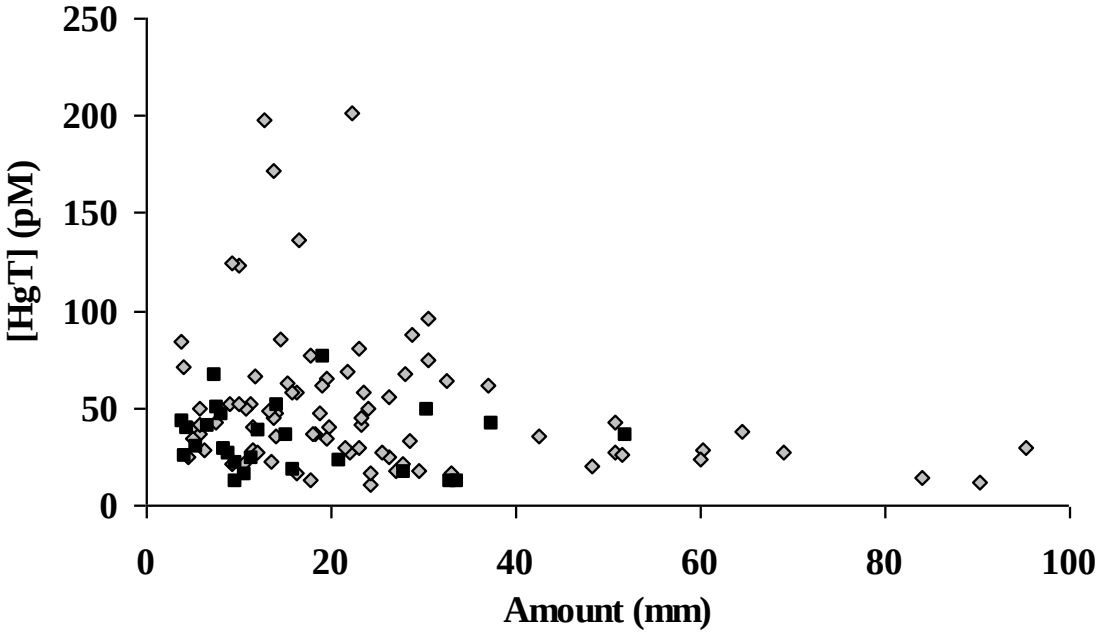


Figure 8: Combined THg data from previous rain study and current rain study at this location. The grey diamonds are data from the previous study (Parler, 2005), and the black squares are from the current study.



Hydrophilic Mercury

Hydrophilic and hydrophobic Hg complexes were measured using C_{18} solid-phase extraction cartridges to investigate Hg-DOM complexes in rainwater. Solid phase extractions with C_{18} have previously been used to examine Hg-DOM complexes in wastewater, but in these studies Hg was added to experimental solutions. Since this is the first study to report Hg separation using C_{18} cartridges at natural levels of Hg, a series of experiments were conducted to ensure the accuracy of this method. The C_{18} cartridges retain hydrophobic mercury complexes, and allow hydrophilic mercury complexes to pass through. Various blanks and solutions were tested before cartridges were used on rainwater samples. MQ water and synthetic rain water used as blanks did not acquire detectable Hg after passing through the cartridge suggesting that contamination of the cartridges was not occurring. Mercury was also spiked into solutions with the known Hg ligands chloride and oxalate. Mercury complexed to these ligands should be present in the hydrophilic fraction and can therefore be used to validate the extraction method. Total dissolved mercury measured before and after passing these solutions through a C_{18} cartridge recovered an average of 102 % of the Hg as hydrophilic complexes. Hsu and Sedlak (2003) validated the use of C_{18} cartridges performing recovery experiments with $HgEDTA^{2-}$ solutions where 104% of the Hg was recovered as hydrophilic.

When attempting to revalidate the C_{18} method at a later date only 54% of the Hg passed through. This lack of recovery occurred on three separate occasions, in July, August and September of 2008. A fourth attempt in September passed 97% of the Hg through the cartridge, with the same experimental conditions as the previous attempts. When additional experiments were performed, recoveries were always close to 100%. Several possibilities were tested to

investigate why recoveries were low during July through September, but no definite conclusion was made. Because rain data was consistent, it was probably not affected by this issue, but could be because no reason was discovered for the problem, so it can't be ruled out.

The total dissolved hydrophilic mercury (hydrophilic TDHg) was determined for 21 rain events by measuring total dissolved mercury (TDHg) before and after passing rainwater through a C_{18} cartridge. The hydrophilic TDHg concentration subtracted from the initial TDHg concentration yields the hydrophobic TDHg concentration. The volume weighted concentration of hydrophilic TDHg was 13.0 ± 1.6 pM, and hydrophilic TDHg was approximately 47% of TDHg (Table 12).

The hydrophilic labile Hg was found for seven rain events in addition to measuring TDHg before and after extraction by measuring the labile Hg before and after passing rainwater through a C_{18} cartridge. The volume weighted concentration of hydrophilic labile Hg was 7.8 ± 2.0 pM, and hydrophilic labile Hg was approximately 48% of the labile Hg (Table 13). An example of a hydrophobic labile complex could be a weakly bound mercury-organic complex. However, when this method was tested in July, 2008 only 62% of a labile Hg synthetic rainwater solution was recovered after passing it through a cartridge. This result occurred about the same time as the other cartridge problems were occurring with TDHg, suggesting that they may be related.

These extractions are potentially useful in examining Hg complexation since the hydrophobic fraction should only contain Hg-DOM complexes, and the hydrophilic fraction could also contain some weak Hg-DOM complexes. A better understanding of DOM influences in rainwater is essential to be able to predict the reactivity of mercury when it is deposited to

surface waters. This could possibly have an effect on important processes in surface waters, such as methylmercury production and/or photochemical redox reactions.

Table 12: Concentrations (pM) of TDHg before and after (Hydrophilic TDHg) passage through a C_{18} cartridge. % Hydrophilic TDHg is the percent TDHg that was hydrophilic.

Rain Event	TDHg (pM)	Hydrophilic TDHg (pM)	% Hydrophilic TDHg
E721	30.7	15.2	49.6
E727	12.3	6.1	49.6
E728	26.5	8.8	33.2
E729	9.8	2.2	22.9
E733	12.8	6.7	52.0
E734	11.6	6.7	57.6
E735	46.4	23.5	50.6
E736	15.8	6.2	39.4
E737	36.7	18.1	49.2
E738	17.0	6.3	37.2
E739	19.8	7.5	37.7
E740	22.5	13.3	59.2
E742	32.6	15.3	46.8
E745	22.0	11.3	51.4
E746	19.5	10.3	52.7
E747	70.4	33.3	47.2
E748	53.8	29.7	55.3
E762	17.4	8.8	50.4
E765	30.3	13.5	44.7
E766	26.9	14.3	53.0
E767	41.4	18.2	43.9

Table 13: Concentrations (pM) of labile Hg before (Labile Hg) and after (Hydrophilic Labile Hg) passge through a C_{18} cartridge. % Hydrophilic Labile Hg is the percent hydrophilic Hg that was labile. NA = not analyzed

Rain Event	Labile Hg (pM)	Hydrophilic Labile Hg (pM)	% Hydrophilic Labile Hg	Chloride Ion (µM)
E721	20.9	7.4	35.4	NA
E727	4.6	2.2	46.9	73
E728	11.9	4.5	37.7	7
E729	5.8	1.6	27.6	1
E733	10.3	4.6	44.8	152
E734	9.0	8.6	95.3	179
E735	35.6	18.1	50.7	19

Competitive Ligand Exchange Titrations

The competing ligand glutathione (GSH^{3-}) was titrated into rainwater to further investigate the strength of Hg(II) complexes in rainwater. Glutathione is a sulfur containing tripeptide that forms hydrophilic complexes with mercury, therefore as more GSH^{3-} is added to solution more Hg(II) should leave its ambient rain complex to form a new complex with GSH^{3-}. At a certain concentration one component will be limiting and the % hydrophilic TDHg will level off as seen in Figure 9. As the concentration of GSH^{3-} increases, the percent hydrophilic mercury increases, demonstrating that the mercury in the rain sample forms complexes with GSH^{3-}. The percent hydrophilic mercury leveled off between 40 and 45 percent of the total mercury suggesting that there are hydrophobic complexes in rain, which are most likely Hg-DOM complexes which are too strong to be broken down by the completing ligand. From this titration, a complexation constant can be estimated for Hg(II) complexes in rainwater, but because of the insufficient knowledge of the characteristics of DOM in rainwater and the exact stoichiometry of the complex, an exact constant cannot be obtained.

When this titration was repeated for other rain events, the same trend of rising percent hydrophilic mercury followed but a plateau was not observed. Instead, a dip in the trend occurred around the 25 nM GSH^{3-} concentration (Figure 10). This was observed in 5 titration attempts following titration of E747. Upon further investigation of these samples, it was observed that E747 has the highest pH of all rain events with which titrations were attempted (Table 14). At different pHs, mercury in solution will change how it binds to GSH^{3-} (Oram et al., 1996), but the changes observed in this study are not consistent with Oram et al (1996). The pH of E747 may have been high enough where all mercury complexes were one mercury bound

to one glutathione ligand (HgHL), whereas the lower pHs of other rain events may have allowed not only that complex, but also the complex of one mercury bound to two glutathione ligands to form ($Hg(HL)_2$, $\log \beta = 52.29$). The GSH^{3-} concentration where the dip is observed may be where the conversion of mercury bound from one ligand to two ligands occurs. This trend may not be seen in surface waters because these waters have even higher pH values.

With more investigation, this method could be used to measure the complexation strength of Hg(II) complexes in rainwater, which would enable a comparison between the relative strength of Hg-DOM in rainwater and surface waters. This information would be very useful because these complexes are likely influencing or even controlling the reactivity of rainwater Hg when it enters surface waters.

Table 14: Rain events with which titrations were performed and their respective pHs.

Rain Event	pH
E747	4.8
E752	4.3
E757	4.3
E759	4.4
E760	4.2
E766	4.3

Figure 9: % hydrophilic Hg as a function of increasing concentration of GSH^{3-} with rain event E747. Error bars represent the standard deviation of duplicate samples.

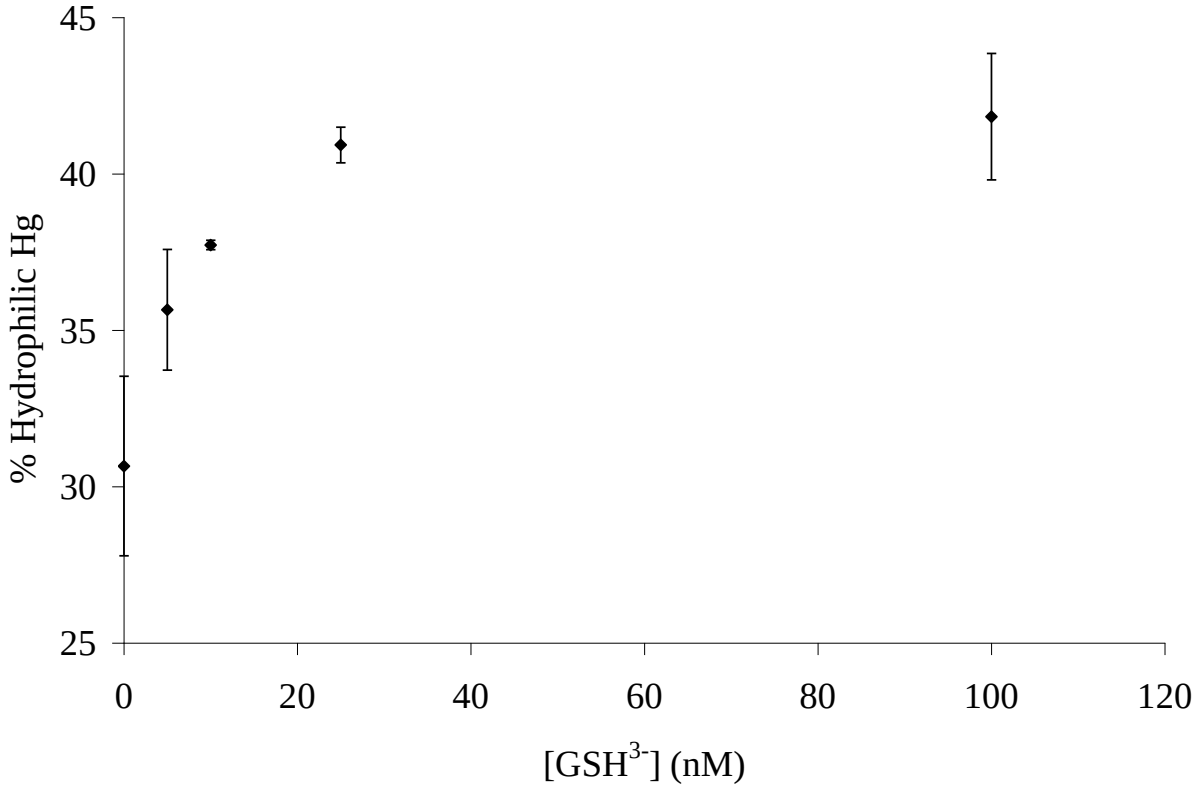
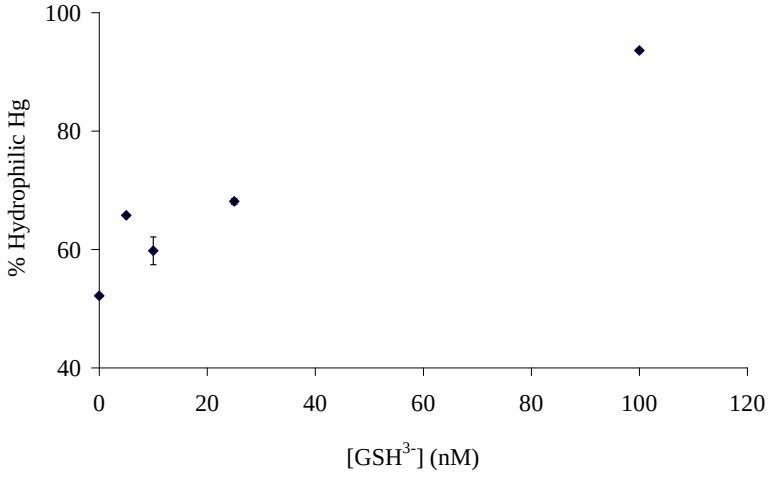
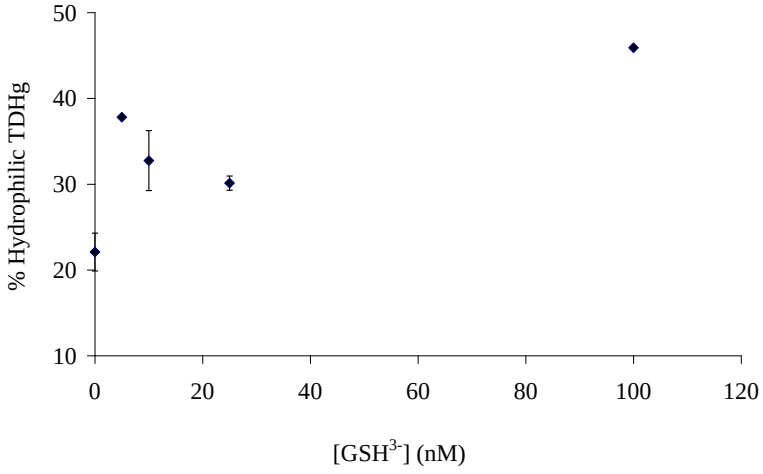
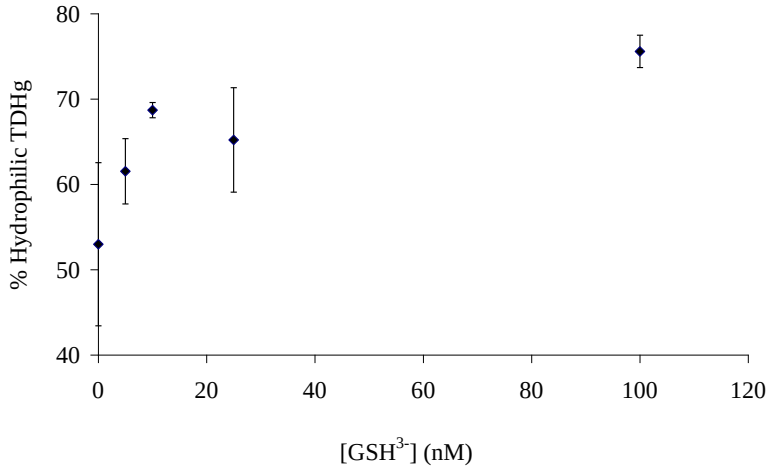
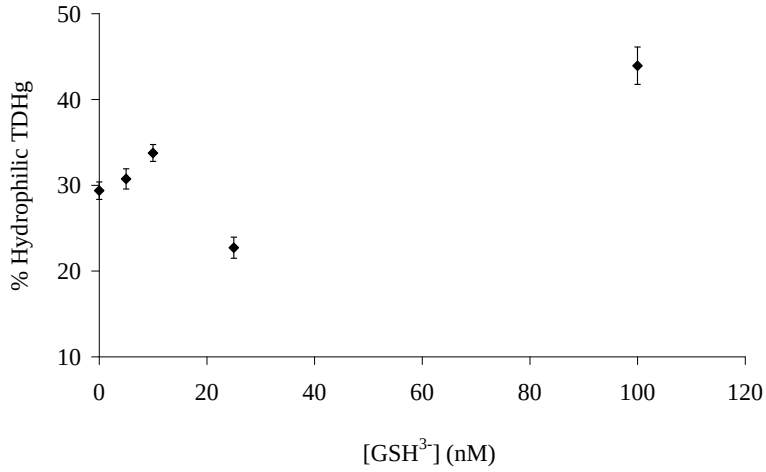


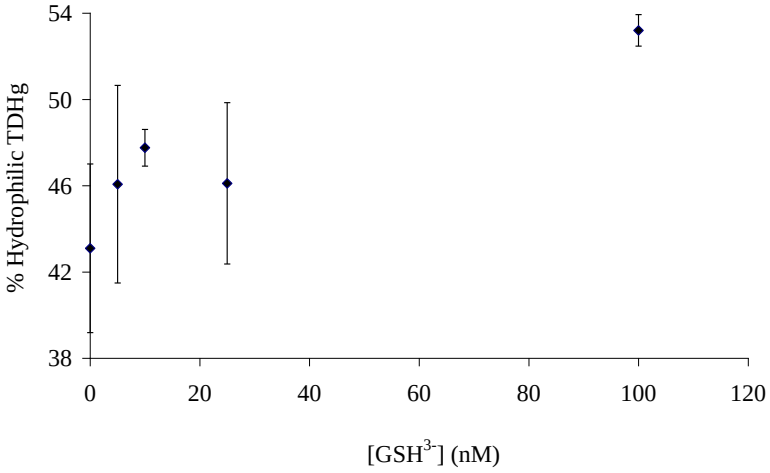
Figure 10: % hydrophilic Hg as a function of increasing concentration of GSH^{3-} with rain events E752, E757, E759, E760 and E766 respectively. Error bars represent the standard deviation of duplicate samples. Note that each graph has a different scale for the x-axis.






80
70
60
50
40
% Hydrophilic TDHg
0
20
40
60
80
100
120
[GSH3-] (nM)


50
40
30
20
10
% Hydrophilic TDHg
0
20
40
60
80
100
120
[GSH3-] (nM)


54
50
46
42
38
% Hydrophilic TDHg
0
20
40
60
80
100
120
[GSH3-] (nM)

Photochemistry Experiments

Rain Photochemistry

Photochemistry experiments were performed on eight filtered rain events and seven unfiltered rain events from June 2007 through February 2008 to determine the influence of sunlight on the speciation of mercury in rainwater. Light can facilitate the oxidation of Hg^0 and the reduction of Hg(II) in surface waters. It is a balance of these oxidation and reduction reactions which control the net amount of DGHg and Hg(II) complexes present. Photochemical reactions also have the potential to change the complexation and reactivity of Hg(II) complexes. Rainwater DOM is very photoreactive (Gordon, 2006), which could result in mercury photochemical reactions driven by the coupling of DOM and light. While the photoreactivity of surface waters is well studied, very little is known about photochemically driven reactions in rainwater. Also, this study found that labile Hg concentration and percent labile of TDHg are higher in the afternoon hours when photochemical reactions occur, compared to the dark, early morning hours. Therefore, rainwater photochemical experiments were conducted where total dissolved Hg (TDHg), labile Hg, and in some cases DGHg were collected before the experiment (Init), after 6 hours in the light (Irr), and after 6 hours in the dark (Dark). Light and dark samples were kept under the same temperature conditions throughout the duration of the experiments.

Labile Hg concentrations decreased in the dark controls in the photochemistry experiments with filtered rain during the six hour irradiation period (Figure 11, Table 17). Labile Hg concentrations in irradiated samples either did not change, or increased relative to dark control samples, indicating photo-production of labile Hg. In all experiments there was a

loss of labile Hg in dark treatments indicating that the labile fraction of Hg is rapidly (over a period of hours) converted to non-reactive species. The concentration of labile Hg in rainwater is a function of both production and loss of these labile Hg complexes. The larger concentration of labile Hg in the light treatments relative to the dark controls suggests that photochemical reactions are contributing to the production of labile Hg complexes. TDHg values did not change from initials in either irradiated or dark samples indicating that there was not a loss of Hg to the bottle wall and that contamination was not an issue (Table 17). The ancillary data for these rain events (Table 15) revealed a weak correlation ($p = 0.108$) of chloride concentration to delta (light-dark) labile Hg concentration. No other correlations were found between the ancillary data and delta labile Hg concentration or delta percent labile Hg.

Labile Hg concentrations did not follow a consistent pattern in the photochemistry experiments with unfiltered rain (Figure 12, Table 18). In two experiments labile Hg concentrations in the irradiated sample increased compared to the initial, in three experiments it stayed the same, and in two experiments it decreased. For the dark labile Hg samples, in four experiments the dark sample decreased compared to the initial, in two experiments it stayed the same, and in one experiment it increased. TDHg values did not change in the dark compared to the initial, but the irradiated TDHg values were inconsistent (Table 18). In four experiments, the light TDHg samples did not change compared to the initial, in two experiments the TDHg increased, and in one experiment the TDHg decreased. Because results from filtered and unfiltered rain were different, rainwater particles must play a role in the degradation of labile Hg. No correlations were found ($p > 0.1$ for all) between the ancillary data and delta labile Hg concentration or delta percent labile Hg (Table 16). Particulate Hg was only measured in E733 through E736, and did not show any relation either ($p > 0.1$).

Dissolved gaseous mercury (DGHg) was analyzed on seven photochemistry experiments to see if DGHg would be produced in rain water after irradiation, as it has been observed in surface waters (Amyot et al. 1994). However, no DGHg production was observed. It has been shown that oxidation of Hg^0 and reduction of Hg(II) simultaneously occur in natural waters (Whalin et al. 2007, Lalonde et al. 2001, Bonzongo & Donkor, 2003) and are both photochemically mediated processes in some natural waters (Whalin et al, 2007). Therefore, the observation that the DGHg concentrations in light were not greater than the dark, does not necessarily mean that DGHg isn't being produced. It could mean that the oxidation and reduction processes are occurring at similar rates, resulting in no net production of DGHg in rainwater.

Figure 11: Initial, 6 hr irradiated and 6 hr dark % labile Hg values using filtered rain. % labile Hg is the percent of total dissolved Hg that is labile. The labels on the x-axis are the numbers of the rain events.

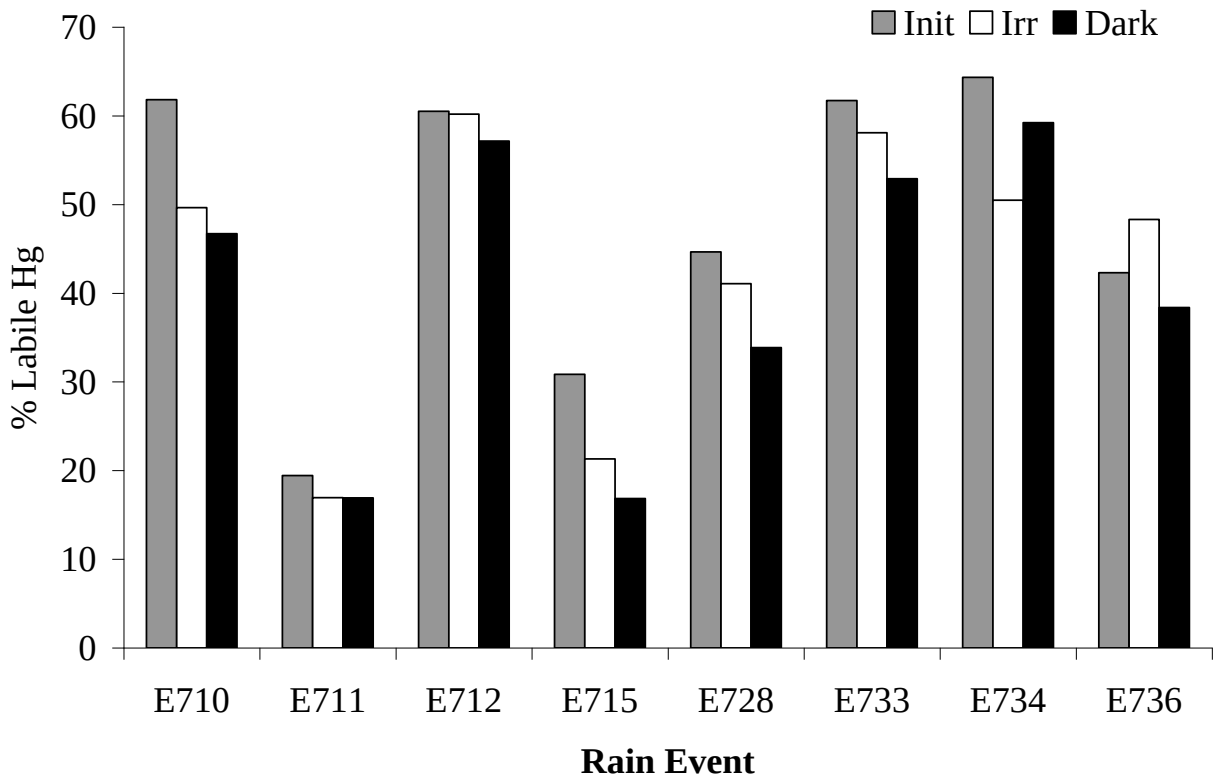


Table 15: Ancillary data for rain events used for filtered photochemistry experiments. NA = not analyzed.

Event	E710	E711	E712	E715	E728	E733	E734	E736
Storm Type	Marine	Marine	Marine	Marine	Terrestrial	Coastal	Mixed	Mixed
Amount (mm)	16	14	33	26	12	11	33	28
pH	4.8	4.4	5.4	5.3	4.5	4.6	5.1	4.6
H_2O_2 (µM)	4.1	12.0	5.4	5.2	16.0	12.9	8.5	3.9
DOC (µM)	18.6	55.3	3.0	14.5	46.3	18.7	7.3	18.5
Cl^- (µM)	10.4	9.1	12.9	4.9	7.2	152.5	178.8	34.4
NO_3^- (µM)	2.8	7.7	1.5	1.6	8.7	6.0	2.9	8.4
SO_4^{2-} (µM)	2.2	10.0	1.1	0.7	11.4	12.3	6.4	7.2
Integrated Fluorescence (QSE)	1.2E4	1.6E4	5.4E4	NA	2.9E4	2.1E4	2.8E4	1.9E4
Δ Light-Dark:								
% Labile Hg	2.9	0.0	3.1	4.5	7.2	5.2	-8.7	9.9
Labile Hg(pM)	0.7	-0.2	0.8	0.8	1.1	0.4	-0.9	1.6

Figure 12: Initial, 6 hr irradiated and 6 hr dark % labile Hg values using unfiltered rain. % labile Hg is the percent of total dissolved Hg that is labile. The labels on the x-axis are the numbers of the rain events.

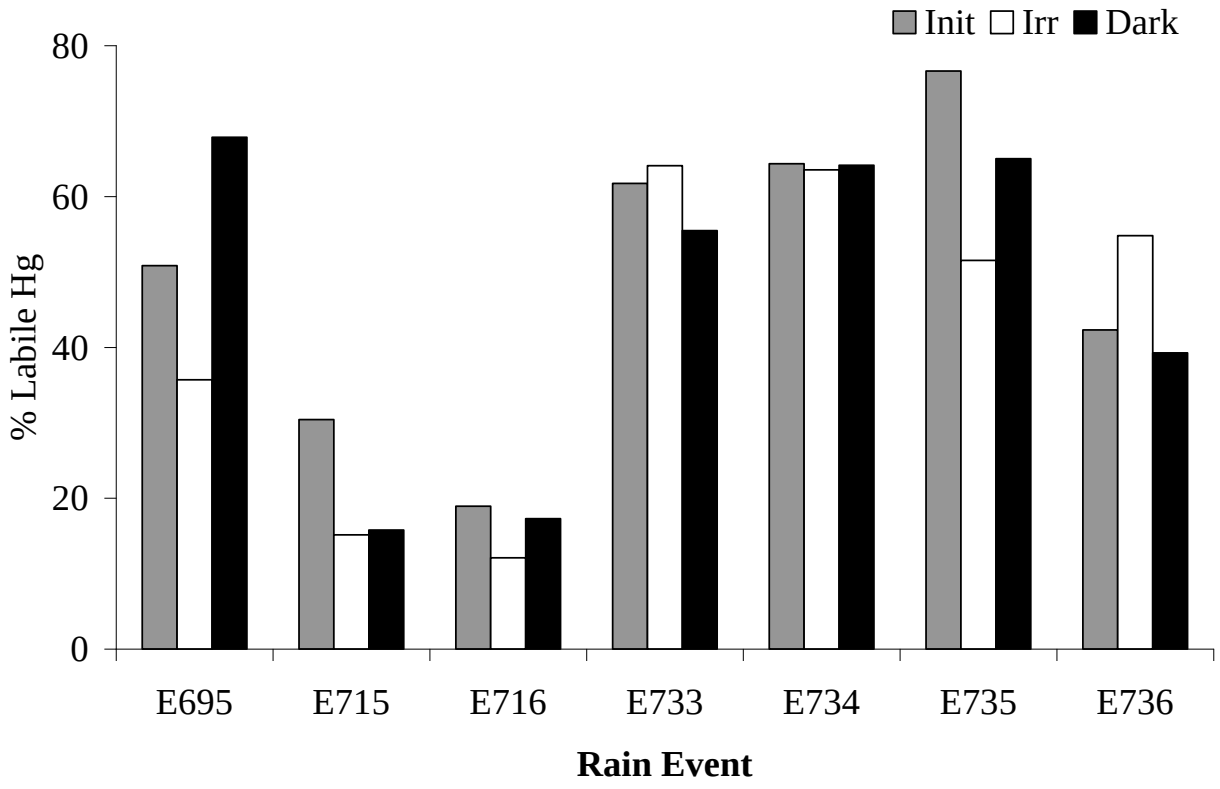


Table 16: Ancillary data for rain events used for unfiltered photochemistry experiments. NA = not analyzed.

Event	E695	E715	E716	E733	E734	E735	E736
Storm Type	Mixed	Marine	Marine	Coastal	Mixed	Marine	Mixed
Amount (mm)	36	26	15	11	33	30	28
pH	5.2	5.3	5.0	4.6	5.1	5.0	4.6
H_2O_2 (µM)	7.1	5.2	6.8	12.9	8.5	6.8	3.9
DOC (µM)	108.4	14.5	13.7	18.7	7.3	12.0	18.5
Cl^- (µM)	116.4	4.9	61.0	152.5	178.8	18.6	34.4
NO_3^- (µM)	4.0	1.6	2.9	6.0	2.9	3.2	8.4
SO_4^{2-} (µM)	12.0	0.7	3.4	12.3	6.4	3.4	7.2
Integrated Fluorescence (QSE)	1.2E4	NA	12.5E4	2.1E4	2.8E4	1.4E4	1.8E4
Δ Light-Dark							
%Labile Hg	-32.1	-0.6	-5.2	8.6	-0.6	-13.5	15.5
Labile Hg(pM)	-0.4	-0.3	-0.8	0.8	-0.1	-9.1	3.2

Table 17: Labile and TDHg values (pM) from filtered rain photochemistry experiments. Init = initial samples, Irr = irradiated samples

	Labile Hg			TDHg		
Event	**Init**	**Irr**	**Dark**	**Init**	**Irr**	**Dark**
E710	8.4	6.5	5.8	13.6	13.1	12.3
E711	4.9	3.9	4.1	25.4	23.0	24.0
E712	5.3	4.9	4.1	8.8	8.2	7.2
E715	6.3	4.3	3.5	20.4	20.0	20.7
E728	11.9	9.9	8.8	26.5	24.2	25.9
E733	7.6	6.5	6.1	12.3	11.2	11.6
E734	6.9	5.7	6.6	10.7	11.4	11.1
E736	7.3	8.1	6.5	17.4	16.7	16.9

Table 18: Labile and TDHg values (pM) from unfiltered rain photochemistry experiments. Init = initial samples, Irr = irradiated samples

	Labile Hg			TDHg		
Event	**Init**	**Irr**	**Dark**	**Init**	**Irr**	**Dark**
E695	5.5	6.7	7.1	10.9	18.9	10.5
E715	5.3	2.5	2.8	17.4	16.8	18.0
E716	2.2	2.9	2.1	11.7	23.8	12.0
E733	7.6	7.1	6.3	12.3	11.1	11.3
E734	6.9	6.6	6.5	10.7	10.4	10.1
E735	35.6	18.4	27.5	46.4	35.7	42.3
E736	7.3	9.8	6.6	17.4	17.8	16.7

Black River Photochemistry

Experiments previously described in this study were conducted to examine the speciation of Hg in unaltered rainwater samples and under photochemically manipulated conditions. Experiments were also conducted to examine the reactivity of freshly added mercury, either from rainwater or in a spike solution to simulate rainwater when it mixes with surface waters. This mixing results in a drastic change in the chemical environment of the mercury resulting in reactions which change the complexation of mercury. Another set of experiments were conducted using water from the Black River, a tributary of the Cape Fear River in North Carolina that has dark, organic-rich fresh water. The river has a moderately high DOC concentration (~15 mgL^{-1}). River water was collected using a polypropylene carboy at a location about 10 miles north of where the Black River meets the Cape Fear River.

Initial experiments were conducted to examine the photochemical reactivity of this black river water that had not been amended with either a mercury spike or rainwater. This provides a comparison between the photochemical behavior of Hg in surface water and rainwater. It also provides comparative information to be used in experiments where Hg was amended to river water. River water photochemistry experiments were carried out with the same procedure as rain water. Three experiments were performed with filtered river water, and two were performed with unfiltered river water collected between July and October 2007. Labile Hg, TDHg, and in most cases DGHg were analyzed. These experiments were performed to observe the impact of light on mercury speciation in a fresh-water black river.

Dissolved gaseous mercury (DGHg) was collected on two filtered and two unfiltered experiments (Figure 13). On average, DGHg was approximately 5 times higher in irradiated

samples than the dark controls for filtered and unfiltered Black River water. This is consistent with results from Amyot et al (1994), in which the DGHg was 2.4-8.9 times higher in irradiated samples than dark controls in lake water in Ontario, Canada and also with Zhang and Lindberg (2001) where DGHg increased approximately 6 times in the light compared to dark control samples in Oak Ridge, TN pond water.

Labile mercury was measured for all Black River photochemistry experiments (Figure 14). The % labile mercury concentrations in dark control samples varied compared to initial labile mercury concentrations, indicating that labile mercury was not stable over 6 hours for filtered and unfiltered Black River water. Irradiated labile mercury concentrations increased relative to the dark controls in every experiment with filtered and unfiltered black river water. This indicates that light produces labile Hg in river water, which was also observed in rainwater. This is one of the first studies to investigate labile mercury photochemistry in a natural water body. Whalin and Mason (2006) and Whalin et al (2007) performed experiments investigating reactive (labile) mercury photochemistry in waters from a freshwater river in the Chesapeake Bay watershed and from seawater from the New Jersey shore. However, the water samples were spiked with $^{199}Hg^{II}$ and $^{202}Hg^{0}$ to investigate redox processes, so its results are not comparable to the results from this study.

Initial, irradiated and dark total dissolved mercury samples were within 10 percent of each other (the precision of the method), indicating that contamination or loss to the sides of the bottles was not occurring in these experiments. There was no consistent difference between filtered and unfiltered Black River photochemistry experiments.

Figure 13: Initial, 6 hr irradiated and 6 hr dark dissolved gaseous mercury concentrations (pM) from Black River. F represents filtered river water, and UF represents unfiltered river water.

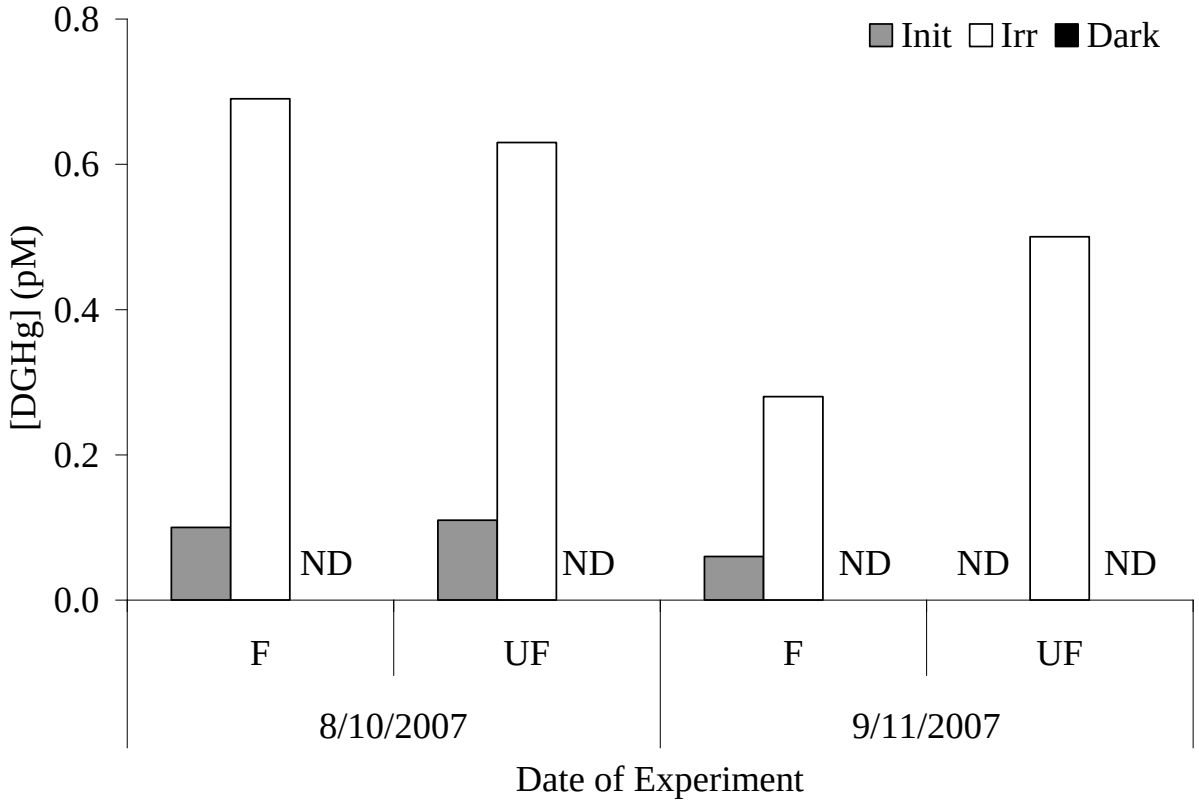
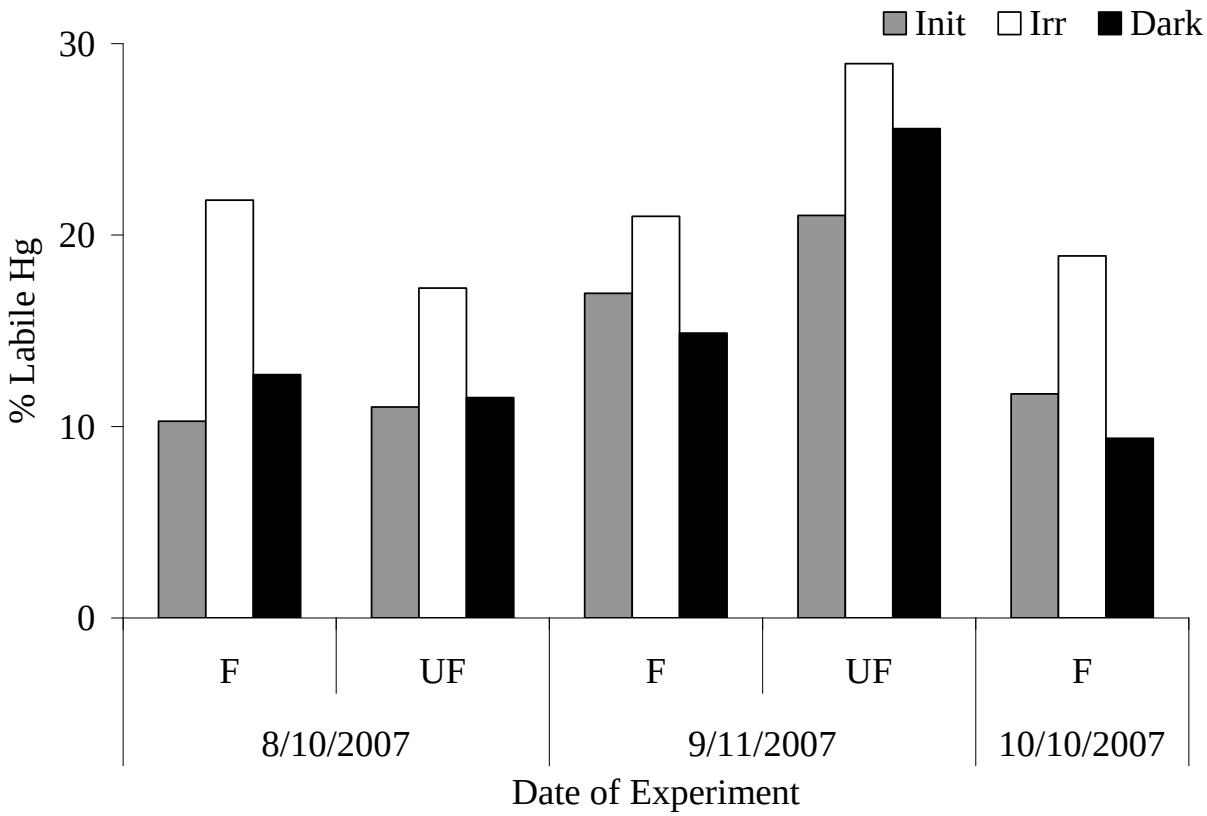


Figure 14: Initial, irradiated and dark % labile mercury values from Black River photochemistry experiments. % labile Hg is the percent of TDHg that is labile. F represents filtered river water, and UF represents unfiltered river water.



Mixed Photochemistry

Five photochemistry experiments were performed with "mixed" water, where fresh filtered rain water was mixed 1:1 with filtered water from the Black River. Five mixing experiments were performed from Sept. 12, 2007 to Sept. 27, 2007. These mix experiments were performed in order to investigate the changes in labile mercury from rain as it mixes with river water, as it would occur naturally in the environment.

Labile mercury and TDHg in mixed samples were always within 1 pM and 2 pM respectively of what would be predicted based on dilution just after mixing (Tables 19 and 20), indicating that labile mercury complexes in rain did not rapidly form Hg-DOM complexes with abundant organic matter in the Black River. Two sets of 6 hour incubations were performed in order to determine if the formation of the Hg-DOM complexes are light driven. The percent labile in both light and dark treatments were not reduced to the level observed in unaltered river water (Figure 15), indicating that the formation of strong Hg-DOM complexes is not a light driven reaction.

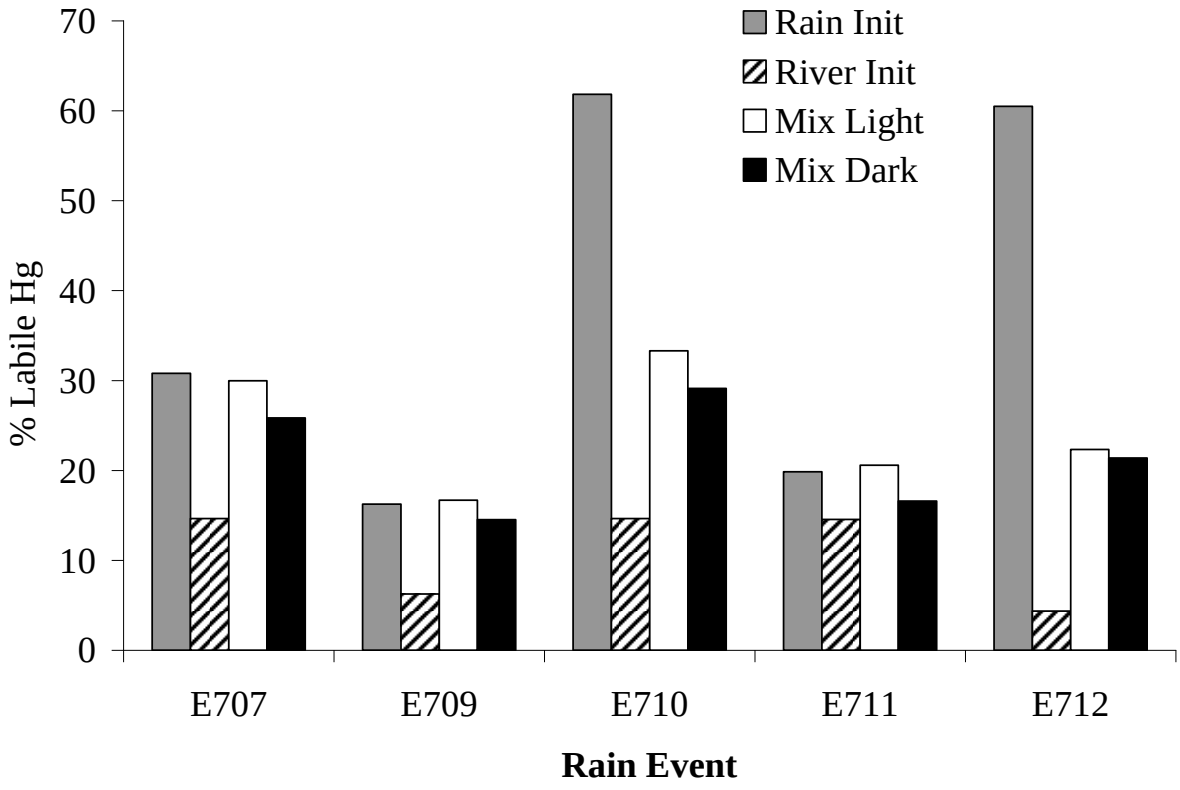
Table 19: Labile Hg values (pM) of rainwater, river water, rain and river mixed (1:1), and the predicted value of the mix based on dilution.

Rain Event	Rain	River	Mix	Predicted
E707	4.6	1.0	3.1	2.8
E709	6.3	0.6	4.2	3.4
E710	8.4	1.2	3.2	4.8
E711	5.0	1.1	3.4	3.1
E712	5.3	0.5	2.6	2.9

Table 20: TDHg values (pM) of rainwater, river water, rain and river mixed (1:1), and the predicted value of the mix based on dilution.

Rain Event	Rain	River	Mix	Predicted
E707	15.0	6.9	11.3	11.0
E709	38.6	9.5	22.0	24.0
E710	13.6	8.3	12.5	10.9
E711	25.4	7.8	16.1	16.6
E712	8.8	10.3	9.7	9.6

Figure 15: Percent Labile Hg in rain water: river water 1:1 mix experiments. The x axis shows each rain event the river water was mixed with. The gray and slashed bars are rain and river initial values respectively, the white bars represent the mixed water after 6 hours of irradiation, and the black bars represent the mixed water after 6 hours in the dark.

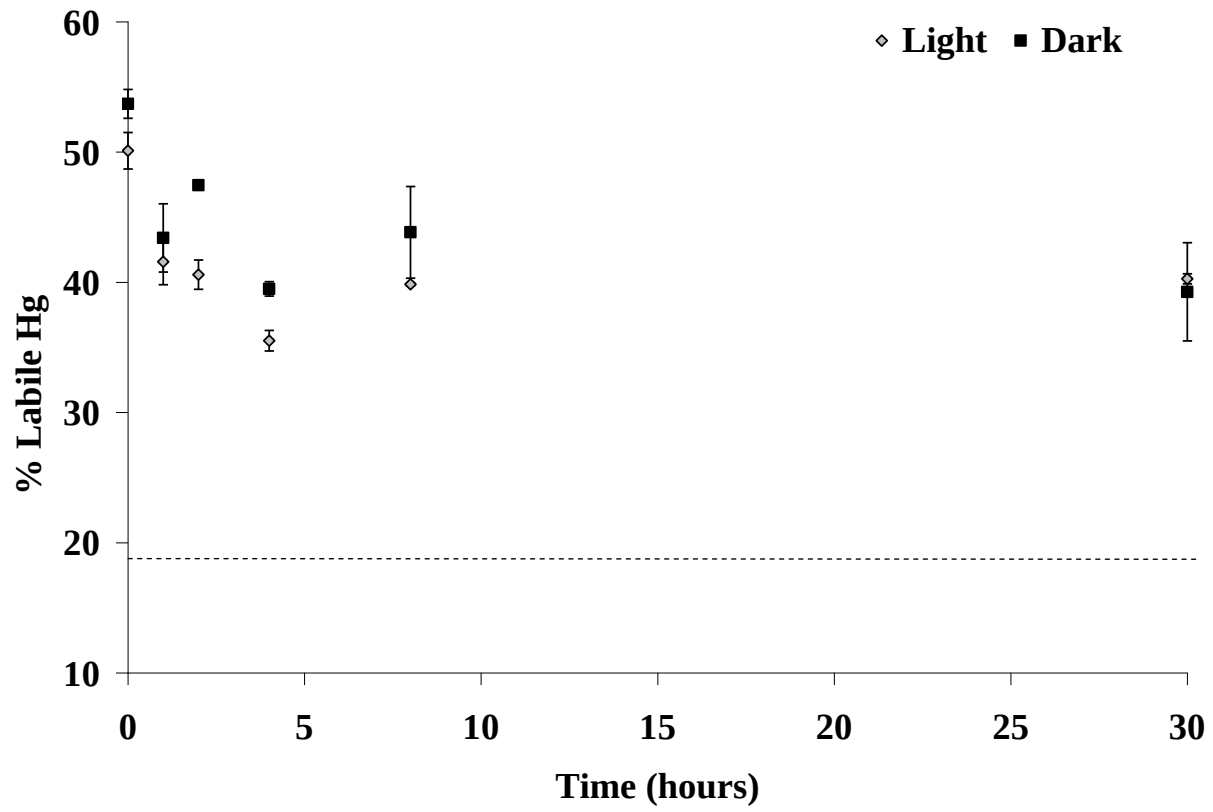


The mixing experiments indicate the reaction kinetics for conversion of labile Hg complexes in rainwater to non-labile Hg complexes was relatively slow. To investigate this further, an experiment was done in which an inorganic mercury spike was added to Black River water and the concentration of labile mercury was measured over 30 hours (Figure 16). The inorganic Hg spike was used to simulate labile Hg entering surface waters from rain, since actual rainwater could not be used due to volume limitations. For this experiment, 10 pM mercury nitrate was spiked into Black River water and then irradiated for 30 hours, with samples taken periodically throughout the irradiation period. Dark controls were also measured.

The river water had approximately 18% labile mercury before mercury was spiked into the sample. As soon as the sample was spiked, the sample had approximately 50% labile mercury. After 5 hours the percent labile mercury in the irradiated samples leveled off between 35 and 40%, which was only slightly lower than the percent labile mercury in the dark samples which were between 39 and 44. Because the light and the dark concentrations are so similar, this is not a photochemically driven process. This is significant because it suggests that rainwater mercury entering surface waters remains in a reactive form for significant periods of time even in the presence of the very high DOM levels found in the Black River. The presence of reactive mercury species has been suggested as the driving species in oxidation-reduction reactions in

surface waters (Whalin et al., 2007), and could be an important factor in the production of methylmercury.

Figure 16: Photochemistry of Black River water with a ten picomolar labile mercury spike. The gray diamonds represent irradiated values, and the black squares represent dark control values. The dashed line represents the percent labile mercury of river water before mercury was spiked into it.



Intense UV Oxidation

Standard mercury analysis methods utilize bromine monochloride to oxidize organic matter, which if present at the time of analysis could result in an underestimate of mercury concentrations. To examine if BrCl oxidizes all of the organic matter in rain, thereby releasing all complexed Hg(II) into solution for THg or TDHg analysis, some samples were exposed to intense UV oxidation prior to addition of BrCl. The UV oxidation processes ensures that all organic matter in a sample is converted to CO_2. Six rain events were UV oxidized between July and September 2008. Duplicate samples were measured for each of these events, and a blank sample was UV oxidized each time.

All six rain samples exposed to UV oxidation showed no increase in TDHg concentration (Figure 17). The TDHg concentrations before and after UV oxidation are listed in Table 21. A similar study was performed with iron in rainwater (Kieber et al., 2005), where total dissolved iron concentrations (TDFe) were measured in 17 rain samples pre and post UV oxidation. This study showed that TDFe had a range of 5 to 67 % increase relative to initial concentrations after UV oxidation, a much different result than observed for TDHg in this study. Olson et al. (1997) found that DOC concentration was a good indicator of conditions where BrCl oxidation was not

sufficient in releasing all Hg(II) to solution. However, they were using water from the Florida Everglades, where DOC concentrations were greater than 35 mg L^{-1}, whereas the highest DOC concentration in these rain samples was less than 3 mg L^{-1}, so it is not surprising that no change is observed in TDHg when UV oxidation is performed on rainwater.

The time gap between the date of the rain event and the date the UV oxidation experiment was performed had an effect on the change in TDHg. There were four UV oxidation experiments that were performed with rain water that had been sitting for weeks or months in the dark in a refrigerator (Table 22). Because of the limited amount of fresh rain during the drought, older rains that had been filtered on the day of the event and kept refrigerated in the dark were used for these experiments. The rain samples shown in Figure 17 are all fresh rain with a time gap of days rather than months between the date the rain fell, and the date the experiment was performed. Ancillary data for all old and fresh rain events were considered, including DOC, anion, and peroxide concentrations, rain volume, pH and integrated fluorescence, but they did not appear to have an affect on the change in TDHg concentration after UV oxidation. This suggests that time is the controlling factor, demonstrating that as rain sits for extended periods of time the complexation of mercury changes, forming stronger complexes.

Figure 17: TDHg (pM) in UV oxidized fresh rain samples. Experiments were performed within an hour of the end of the rain event. Initial TDHg samples were not UV oxidized. Final A and Final B are duplicate TDHg samples that were UV oxidized in two separate quartz tubes.

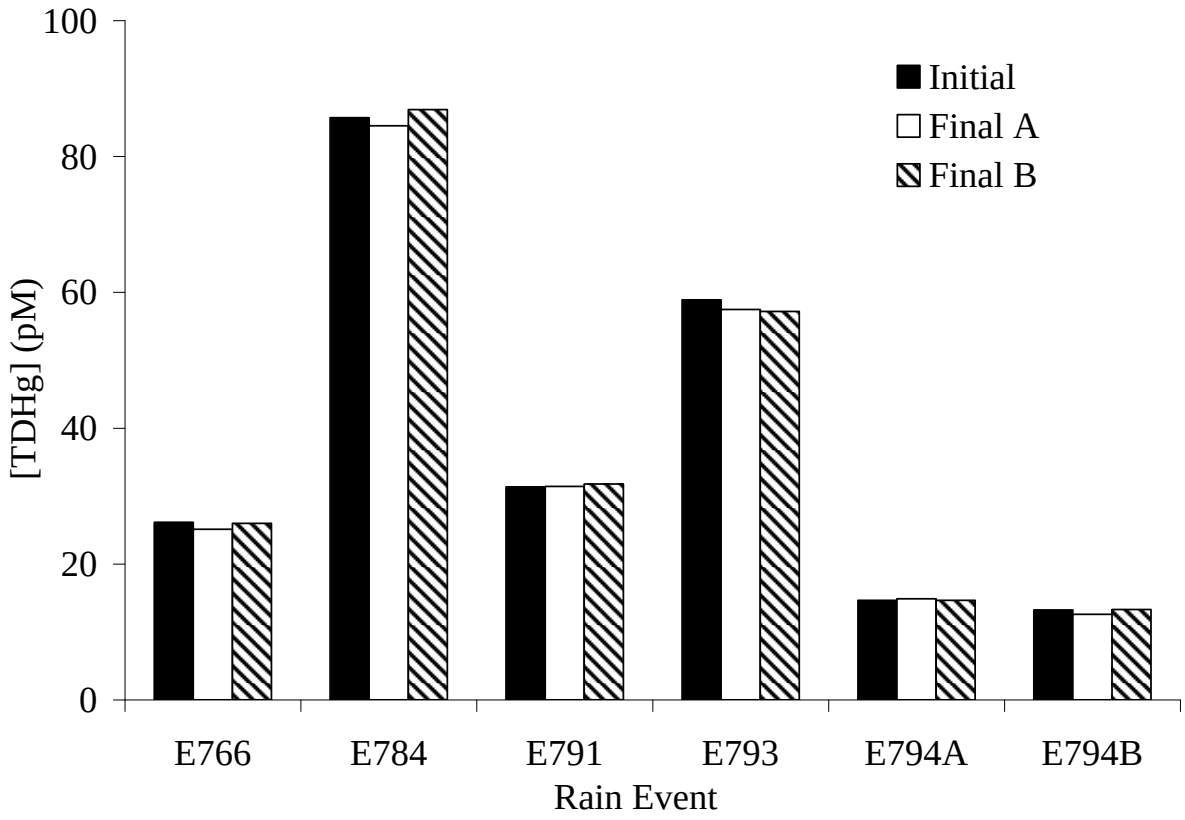


Table 21: Total dissolved mercury concentrations of rain events, pre and post UV oxidation. Standard deviations are given for samples where duplicates were measured. A and B represent duplicate sample concentrations.

Event	E766	E784	E791	E793	E794a	E794b
TDHg pre (pM)	26.1	85.7	31.4	58.9	14.6	13.2
TDHg post (pM)	A: 25.1 B: 26.0	A: 84.5 B: 86.9	A: 31.4 B: 31.8	A: 57.5 B: 57.2	A: 14.9 B: 14.7	A: 12.6 B: 13.3
Average Δ TDHg (pM)	-0.6	0.0	0.2	-1.6	0.2	-0.2
Average % Change	-2.2	0.0	0.7	-2.7	0.9	-2.1

Table 22: UV oxidation of rain events that were not performed immediately after the rain fell.

Event	E734	E738	E746	E749
Date of Event	2/13/2008	3/5/2008	4/3/2008	4/22/2008
Date of Experiment	7/18/2008	7/11/2008	5/12/2008	5/12/2008
TDHg pre (pM)	7.7	11.8	17.8	31.8
TDHg post (pM)	8.6	12.5	20.6	35.9
Δ TDHg (pM)	0.9	0.8	2.8	4.1
% Increase	11.8	6.4	15.7	12.9

CONCLUSIONS / IMPLICATIONS

Rainwater mercury concentrations have been well documented in the US through the NADP rainwater collection sites and other studies (NADP, 2008) but the speciation and reactivity of Hg in rainwater previously had not been investigated. It is crucial to understand the speciation of Hg in rainwater since this will impact its cycling in aquatic systems after deposition. In this study, the speciation of Hg in rainwater was examined by measuring DGHg, THg and TDHg to examine the oxidation state of mercury, and labile Hg and hydrophilic Hg was used to quantify the importance of inorganic and organic Hg^{2+} complexes. The reactivity of Hg after deposition was also examined by exposing it to light, and mixing rainwater with river water in both the presence and absence of light.

Dissolved gaseous mercury has not been accurately quantified in rainwater since measurements need to be conducted immediately after rain deposition. Many programs, such as the National Atmospheric Deposition Program / Mercury Deposition Network (NADP/MDN), collect rain once a week, resulting in any DGHg in that sample degassing by the time total mercury is analyzed and therefore eliminating it from the measured total mercury concentration. DGHg was determined to be less than one percent of the total mercury in rainwater. Because DGHg was found to be such a small percentage of the total mercury, if present at all, it can be assumed that the DGHg contribution is negligible to the overall Hg concentration in rainwater. The production of DGHg in rainwater in photochemistry experiments did not occur, providing further support that DGHg is not an important component of rainwater and that divalent Hg is the dominant form of mercury in rainwater.

The presence of nonreactive and hydrophobic complexes of Hg indicates that Hg-DOM complexes exist in rainwater. These complexes can be strong or weak, and hydrophilic or hydrophobic. These findings lead to a better understanding of the fate of mercury in the environment. Complexation of Hg is dominated by strong Hg-DOM species in most aquatic environments. Rainwater provides a source of mercury which contains both Hg-DOM and Hg-inorganic, reactive species to surface waters. Rain and river water mixing experiments were used to simulate the behavior of rainwater Hg after its deposition to surface waters and showed that labile Hg complexes in rainwater do not rapidly form non-labile complexes when added to river water. This is unexpected due to the high DOC concentration in the river water which results in equilibrium speciation models predicting the dominance of non-labile Hg species. This could mean that there is more labile mercury than previously thought in river water due to the slow kinetic formation of the strong Hg-DOM complexes especially after recent rain deposition. The presence of these reactive species will likely impact the transport and fate of rainwater deposited Hg on aquatic systems. Rainwater Hg could also provide a pool of Hg which is available for Hg methylation. In addition to this, photochemistry experiments showed that light can produce labile mercury in rain water alone, river water alone, and the two combined, further demonstrating that labile mercury concentrations in rivers are complex and varied, depending on several environmental factors.

While the reactivity of Hg in surface waters has been extensively studied, very limited data was available on the reactivity of Hg in rainwater. This study focused on the speciation of mercury in rainwater, so more can be understood about its reactivity and subsequent toxicity. The information presented in this thesis gives a better understanding of how mercury in rainwater is related to DOM, factors that influence these relationships, and what effects that has

when mercury from rainwater enters aquatic systems. There is still much to learn about these topics, such as what specifically controls the formation of strong Hg-DOM complexes in rainwater mixed with river water, but this new information gives a good starting point.

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